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Ultrathin Membranes for Treating Metal Finishing Effluents by Reverse Osmosis

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ULTRATHIN MEMBRANES FOR TREATING METAL FINISHING EFFLUENTS BY REVERSE OSMOSIS

by

North Star Research and Development Institute
3100 Thirty-Eighth Avenue South
Minneapolis, Minnesota 55406

through

The State of Minnesota Pollution Control Agency

for the

Environmental Protection Agency

Industrial Pollution Control Section

Project 12010 DRH

November 1971

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ABSTRACT

Reverse osmosis has been examined as a process for treating metal finishing wastewaters. Seventeen different membranes were evaluated for the separations of heavy metal ions, acids, bases, and cyanides from water. They included commercially available asymmetric membranes (approximately 0.002 inch in thickness) and ultrathin membranes (1×10^{-6} to 2×10^{-5} inch in thickness). Experimental results showed that reverse osmosis is feasible and effective in treating these effluents for both pollution control and metal ion and water recovery for possible recycle. Although no one membrane was found effective for all effluents, membranes of five different polymers showed considerable promise.

Simulated acidic nickel, iron, zinc, and copper plating bath rinses were effectively treated by ultrathin membranes of three polymers: cellulose acetate, cellulose methyl sulfonate O-propyl sulfonic acid, and β-glucan acetate dimethylaminoethyl ether. Water fluxes were generally above 30 gallons per square foot (of membrane) per day (gfd) at metal ion rejections up to 99.9 percent.

Simulated chromic acid rinses were effectively treated by ultrathin cellulose methyl sulfonate O-propyl sulfonic acid. This membrane exhibited a water flux of 27 gfd with 95-percent rejection of chromium (at pH 2.5).

The sulfonated polyphenylene oxide was the only membrane to withstand hydrolysis for over 170 hours by a highly alkaline (pH 11.4) copper cyanide solution. The rejection was 98 percent for copper and 93 percent for total cyanide, with a water flux of 45 gfd.

Preliminary engineering considerations on the application of reverse osmosis to the treatment and recycle of rinse waters from an acidic copper (sulfate) plating bath are included.

This report was submitted in fulfillment of Project 12010 DRH under the partial sponsorship of the Environmental Protection Agency.

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SECTION I

CONCLUSIONS

This study has led to the following conclusions regarding the feasibility of treating metal finishing wastewaters by reverse osmosis:

1) The treatment of metal finishing wastewaters by reverse osmosis has been shown to be feasible. Membranes exhibiting water fluxes over 30 gfd have shown excellent rejections of metallic, acidic, or basic solutes. Although no single membrane is capable of adequately treating all types of wastewaters, membranes are available which exhibit excellent rejections and high water fluxes for certain types of wastewaters.

2) The membranes that show the most promise in treating acidic wastewaters containing nickel, iron, zinc, and copper salts are ultrathin cellulose acetate (E 360-60), ultrathin β-glucan acetate dimethylaminoethyl ether, and ultrathin cellulose methyl sulfonate O-propyl sulfonic acid. These membranes are capable of concentrating an acidic copper sulfate rinse solution from one-tenth of one percent to between forty and eighty percent of the original plating bath concentration (51,500 mg per liter Cu) while still maintaining good water fluxes (13 to 25 gfd) and copper ion rejections (>99 percent). In addition to their excellent performance during the treatment of wastewaters containing a single metal salt, these membranes performed similarly for wastewaters containing a mixture of the above metal salts.

3) Three membranes show promise for treating wastewaters containing chromic acid: ultrathin cellulose methyl sulfonate O-propyl sulfonic acid, ultrathin cellulose acetate (E 398-10), and asymmetric cellulose acetate (RO-97). Chromic acid is more easily rejected at pH 5.0 than at 2.5 or less. All three of the above membranes exhibit chromic acid rejections of between 90 and 98 percent with fluxes up to 25 gfd at pH 5.0. At pH 2.5, however, the rejections drop to between 83 and 90 percent. In addition, both cellulose acetate membranes are slowly hydrolyzed at pH 2.5. The cellulose methyl sulfonate O-propyl sulfonic acid membrane, which has exhibited some resistance to hydrolysis in short-term tests, appears to be the best membrane for use at pH 2.5 or lower.

4) An experimental sulfonated polyphenylene oxide membrane (General Electric JEPDM-127) is the only membrane of all those tested that can withstand hydrolysis by a highly alkaline (pH 11.4) copper cyanide solution. This membrane is able to reject over 98 percent of the copper and 93 percent of the total cyanide while maintaining a water flux of 45 gfd.

5) Acids and bases in solution are more difficult to reject than are the metal salts. The order of rejection for three acids and one

base is H_2SO_4 > HCl > HNO_3 > NaOH. Asymmetric cellulose acetate (RO-97) exhibits the best overall rejection of these species, but other membranes also exhibit similarily high rejections for the sulfuric acid.

6) Ultrathin β-glucan acetate dimethylaminoethyl ether is unique among the membranes tested, in that it does not reject the acidic and basic species, and it is the only membrane which exhibits a higher water flux at pH 2.5 than at pH 5.0.

7) The program has shown that reverse osmosis performance of ultrathin membranes can be improved by (a) modifying the chemical composition (degree of substitution), (b) optimizing the annealing conditions, (c) producing as thin a membrane as practical, and (d) using a polysulfone support film. Proper manipulation of these variables can result in higher water fluxes and lower flux declines coupled with the required rejections.

8) Preliminary engineering considerations on the application of reverse osmosis using ultrathin cellulose acetate to the treatment and recycle of waste rinse waters from an acidic copper (as sulfate) plating bath show a 99.8-percent recovery of the copper sulfate and a 99.9-percent recovery of the water.

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16. Abstract:

Seventeen different reverse osmosis membranes were evaluated as to their ability to separate heavy metal ions, acids, bases, and cyanides from metal finishing wastewaters. Although no one membrane was found to be effective for all effluents, membranes of 5 different polymers showed considerable promise. Simulated acidic nickel, iron, zinc, and copper plating bath rinses were effectively treated by ultrathin membranes of cellulose acetate, cellulose methyl sulfonate, O-propyl sulfonic acid, or β-glucan acetate diaminoethyl ether, with water fluxes of 30 gal/ft^2-day and metal ion rejections of 99.9%. Simulated chromic acid rinses, subjected to treatment by ultrathin cellulose methylsulfonate O-propyl sulfonic acid membranes, exhibited a 27 gfd flux, with 95% chromium ion rejection at pH 2.5. These investigations have demonstrated that ultrathin membrane separation performance can be modified by: (1) modifying the chemical composition; (2) optimizing the annealing conditions; (3) producing as thin a membrane as practical; and (4) using a polysulfone support film. Preliminary engineering considerations for reverse osmosis applications to treatment and recycle of acidic copper plating bath rinse waters show a 99.8% copper recovery and a 99.9% recovery of the water. (Lowry-Texas)

are presented ( )

17a. Descriptors

*Reverse osmosis, *Membranes, *Heavy metals, Acids, Alkalis (bases), Ions, Separation techniques, Thin films, Laboratory tests, Performance, Pressure, Temperature, Hydrogen ion concentration, Oxidation, Hydrolysis, Optimization, *Waste water treatment, Water reuse, Industrial wastes

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SECTION II

RECOMMENDATIONS

The overall purpose of this program is to examine reverse osmosis as a process for treating metal finishing wastewaters and to develop the process for industrial application. The major task of this first phase was to evaluate membranes for their effectiveness in this application. The scope of the first phase did not include optimization or extensive engineering consideration. The experimental studies conducted resulted in five potentially effective membranes for reverse osmosis treatment of metal finishing wastewaters, and it is recommended that this program be continued to the field-demonstration phase.

The first task that should be carried out in a second phase of this program is optimization of the reverse osmosis properties of the five membranes found to work effectively on selected metal finishing effluents. These membranes are (1) asymmetric cellulose acetate (RO-97), (2) ultrathin cellulose acetate (E 360-60), (3) sulfonated polyphenylene oxide (JEPDM-127), (4) ultrathin β-glucan acetate dimethylaminoethyl ether, and (5) ultrathin cellulose methyl sulfonate O-propyl sulfonic acid. The following properties must be adjusted for optimum performance.

- The synthesis of the β-glucan dimethylaminoethyl ether and the cellulose methyl sulfonate O-propyl sulfonic acid must be investigated and controlled to produce polymers of known purity and predictable degrees of substitution. Thus, the polymer structure that would give optimum performance would be elucidated.

- Procedures for casting ultrathin membranes in the most applicable configuration (probably tubes) must be optimized to obtain high water flux. Optimization would include investigation of the concentration of polymer casting solution, casting solvents, additives (such as surfactants) to the water or casting solution, and annealing to produce, consistently, a membrane as thin as possible.

- The conditions under which all these membranes will be tested must be optimized with respect to temperature, pressure, and pH. The type of wastewater treated will largely determine these conditions.

The optimization testing would include long-term (up to 500 hours) reverse osmosis tests with simulated or actual metal finishing wastewaters, during which the effects of oxidation and hydrolysis on the membranes would be investigated.

A second step in this proposed phase of the program would include engineering studies, an economic analysis of membrane production, and preparation for a field demonstration. These considerations would lead directly to a third phase, which would consist of small-scale, on-site demonstration.

SECTION III

INTRODUCTION

North Star Research and Development Institute has completed the first year of research on the program "The Use of Reverse Osmosis for Treating Metal Finishing Effluents". The Minnesota Pollution Control Agency, as grantee from the Applied Science and Technology Branch, U.S. Environmental Protection Agency, together with six private organizations, sponsored the work as Program No. 12010 DRH.

This program was designed to serve the needs of the metal finishing industry through improved pollution control and possible conservation of valuable materials. Reverse osmosis offers an efficient and potentially economical method to meet these needs. The first phase of the program, described in this report, consisted primarily of determining which membranes, from commercially available and experimental membranes, were most promising for treatment of metal finishing wastewaters. The most important membrane performance criteria were high rejections of specific components, high water fluxes through the membranes, and low declines in flux during operation.

Technical Background

The metal finishing industry has an ever-growing problem in controlling the effects of its wastewaters. The wastes that cause the problems include rinse waters from metal electroplating solutions and from acid and alkaline cleaning and pickling solutions. These rinse waters, if discharged into the environment without treatment, can pollute our natural resources, inhibit or destroy natural biological activities, and adversely affect materials of construction. Specific examples of these detrimental effects include the toxicity of heavy metals and cyanides to various forms of aquatic life,[1] the deleterious effect of copper and chromium on biological sewage treatment processes (because of their toxicity to the microflora),[2] and the corrosive effects of acids and bases on sewer lines and metal and concrete structures.[3,4]

Metal Finishing Operations

The following metal finishing operations are those most commonly found in the electroplating and metal finishing industry and are the source of the major portion of the waterborne wastes:

(1) Cleaning. Cleaning processes are mainly designed to remove soil, oil, and grease. They are usually of three general types: organic solvent cleaners, acid pickling cleaners, and alkaline cleaners. Organic solvent vapor cleaners are used mainly for oil and grease removal. Acid pickling cleaners are used for removal of oxides, sulfides, and other undesirable surface deposits. They

are generally solutions of sulfuric, hydrochloric, or nitric acid, the strength of which depends upon the metal to be cleaned.

Alkaline cleaners consist of organic emulsion cleaners, alkali soaking cleaners, and alkali electrocleaners. The organic emulsion cleaners are aromatic or aliphatic solvents coupled with an emulisifier. Alkali soaking cleaners consist of sodium hydroxide, orthophosphates, polyphosphates, silicates, carbonates, organic emulsifiers, and synthetic wetting agents. Alkali electrocleaners are similar to soaking cleaners except that they can be used as either anodic or cathodic electrocleaners.

These cleaning methods are not mutually exclusive and are often used in combination.

(2) Plating. In the plating process, the actual deposition of the metal takes place. The material being plated is the cathode in an electrolytic cell. Plating baths can be acidic or alkaline, depending on the metal to be plated, the type of plate desired, and the surface metal on which the plate is to be deposited.

(3) Stripping. Stripping processes are necessary for the removal of undesirable metallic, metallic oxide, or other coatings which may be on the work piece to be plated or otherwise coated. The type of stripping process depends on the film to be removed and the base metal. Most stripping baths are acidic in nature and usually consist of solutions of sulfuric, nitric, hydrochloric, or to a lesser extent, hydrofluoric acids. In addition to the acidic baths, alkaline baths with sodium sulfide, sodium cyanide, and sodium hydroxide may also be used. Electrolytic stripping has been used increasingly in the past few years. In this method, the material to be plated is the anode, usually in baths equivalent to those mentioned above.

Sources and Present Treatment of Wastewaters

Waterborne wastes generated in the above operations include the following:

(1) Rinse waters from plating, cleaning, and other surface finishing operations;

(2) Concentrated plating and finishing baths that are intentionally or accidentally discharged;

(3) Wastes from plant or equipment cleanup;

(4) Sludges, filter cakes, etc., produced by naturally occurring deposition in operating baths or by intentional precipitation in the purification of operating baths, chemical rinsing circuits, etc., when flushed down sewers.

From the viewpoint of the smaller plater, by far the most important of these wastes is the rinse water. It is a constantly flowing, production-connected stream that is generally so large in volume that it cannot be economically impounded for treatment before disposal. This stream is usually concentrated enough to be toxic.

The inactivation or removal of the undesirable constituents from metal finishing wastewaters prior to their disposal is therefore necessary to minimize their detrimental effects on the environment. Several methods exist which accomplish this task with varying degrees of success. The simplest method is the neutralization of an excessively acid or alkaline waste. Inactivation and removal of the metal and cyanide species can be accomplished by oxidation or reduction to a less contaminating state, precipitation to permit removal, or ion exchange for removal or recovery.

Table 1 lists the origin and presently used treatments of the most common types of metal finishing wastewater impurities. Various problems are encountered in the use of any one of these techniques, a few of which include large space requirements, complicated operating procedures, high cost, and insufficient removal of the contaminating species. In addition, the objective of most of the conventional methods of treatment is ultimate disposal or destruction of undesirable constituents, with relatively little attention being given to recovery of the contaminating species or the water.

Research Program

The purpose of the present research program is the examination and evaluation of the reverse osmosis process for treating metal finishing wastewaters. Treatment of these effluents by reverse osmosis could not only render any waste effluents harmless to the environment, but could also permit the reuse of a highly purified product water and the recovery of metal and other values discarded in other treatment processes. Reverse osmosis is also advantageous because of its relatively low space requirements (being modular in design), its adaptability to various processes, its ease of operation, and the possibility of lower operating cost than conventional processes.

Reverse osmosis can be used in combination with existing methods of treatment to increase efficiency, or it can be used alone. In combination with existing methods, it can be used to treat water from a

Table 1. Origin and Present Treatment of Some Metal Finishing Waste Effluents[5]

Type of Impurity in Effluent	Origin	Treatment Alternatives
Acids:		
sulfuric hydrochloric nitric	metal pickling	neutralization with alkali
hydrofluoric	metal pickling	neutralization and precipitation
phosphoric perchloric acetic	pickling, phosphating, polishing	neutralization and precipitation
Alkalies:		
caustic soda sodium carbonate silicates phosphates	cleaning solutions, alkaline pickling solutions	neutralization with acid
Metal Ions:		
precious metals copper nickel	electroplating baths, spent pickles	sedimentation, precipitation with alkali, electrolysis, ion exchange
Cyanides:		
simple cyanides	hardening, cleaning solutions	destruction by alkaline oxidation, precipitation with iron, ion exchange
complex cyanides	electroplating baths	oxidation, precipitation, sedimentation, ion exchange
Chromic Acid:	electroplating, anodizing, polishing, chromating solutions	acid reduction and precipitation with alkali, ion exchange

continuous destruction process for recycling back to the plant operations, or it can increase the metal ion concentration prior to an ion exchange treatment. If used alone on an individual plating line, it can provide rinse water for recycling and the reclamation of metal salts or other chemicals for reuse.

Evaluation of reverse osmosis as a procedure for treating metal finishing wastewaters must begin with the selection and evaluation of the membranes which perform the actual separations. Membranes were chosen and evaluated with respect to their ability to reject a variety of metal salts, acids, and bases while maintaining a high water flux (>20 gfd). Three types of membranes were evaluated in this program: 1) asymmetric, 2) ultrathin, and 3) homogeneous.

An asymmetric membrane has a thin, dense surface layer backed by a thick porous layer. The dense layer (~0.25 micron, 2500 angstroms, or 1×10^{-5} inch thick) is in contact with the feed solution and serves as the barrier to the passage of dissolved materials. The porous layer (~100 microns, 10^6 angstroms, or 0.004-inch thick) provides support for the dense layer and permits the diffusion of the purified solvent into a collecting system. Examples of asymmetric membranes evaluated in this program are Eastman's cellulose acetate RO-97, RO-94, and RO-89.

Ultrathin membranes are homogeneous polymeric films ranging in thickness from 200 Å to 6000 Å ($\sim 1 \times 10^{-6}$ to $\sim 2 \times 10^{-5}$ inch). They are similar in physical structure and have the same function of rejecting dissolved materials as does the dense surface layer of the asymmetric membrane. Ultrathin membranes have no underlying support structures and can therefore be supported on materials different from those of which they are composed. The thickness of the ultrathin membrane is easily controlled by the rate at which it is cast. Since the water flux is inversely proportional to membrane thickness, the ability to control the thickness provides one method of controlling the water flux. In this program, ultrathin membranes were made from commercially available polymers, such as Eastman's cellulose acetate butyrate (EAB-171-5), and from polymers synthesized at North Star, such as cellulose methyl sulfonate O-propyl sulfonic acid.

Homogeneous membranes are differentiated from ultrathin membranes in that they range in thickness from 0.2 mil (5×10^4 Å) to 0.5 mil (12.5×10^4 Å). They are supported on a separate polymeric film in the same manner as the ultrathin membranes. An example of this type of membrane is General Electric's sulfonated polyphenylene oxide (JEPDM-127).

In addition to screening a variety of different membranes, it was important to determine (on a preliminary basis): 1) the effects of operating variables (pressure, temperature, and pH) on the membrane performance; and 2) the effects chemical and physical modifications of the membrane would have on its performance.

In order to screen a maximum number of membranes, short-term (<20 hours) tests were carried out. Longer tests (>100 hours) were conducted only 1) when it was suspected that the composition of the feedwaters might adversely affect the performance of the membrane, or 2) to observe the effects of an increasing feed concentration on membrane performance.

SECTION IV

EVALUATION PROCEDURES

Tests conducted during this report period included screening various types of membrane materials for their effectiveness in treating a variety of simulated metal finishing waste solutions. Also investigated were the effects of operating variables on membrane performance and the optimization of membrane performance by chemical or physical modification.

Sixteen of the twenty-one membranes listed in Table 2 have been tested by reverse osmosis using simulated rinse waters from representative nickel, iron, copper, zinc, and chromium plating baths. The other five membranes had water fluxes less than one gfd or rejections less than ten percent during preliminary tests on sodium chloride solutions and were not tested further. The membranes tested included commercially available asymmetric membranes, ultrathin membranes cast from commercial polymers, and ultrathin membranes cast from polymers prepared at North Star. Appendix A gives the chemical structures of the polymers; Appendix B explains the ultrathin membrane casting procedures; and Appendix C gives the procedures for synthesizing the polymers prepared at North Star.

The simulated plating bath rinse solutions used in the membrane-testing procedures contained the most common as well as the most troublesome metal salts, acids, and bases. Solutions containing nickel, iron, copper, zinc, and chromium metal ions and cyanide ions represented the acid and alkaline electroplating rinses. Solutions containing sulfuric acid, hydrochloric acid, nitric acid, or sodium hydroxide represented the acid and alkaline cleaning and stripping solution rinses. The procedures for preparing the feed solutions are given in Appendix D.

The reverse osmosis tests were carried out in flat cells under 600 psig pressure at 25°C. The test system and flat cell are pictured in Figures 1 and 2, respectively. Appendix E describes the reverse osmosis test system. For most of the tests, the metal ion concentrations in the feed solution were maintained at 100 mg per liter by a recirculating system. The membranes were precompressed with a one-tenth-percent sodium chloride solution followed by testing with solutions containing nickel, zinc, iron, copper, and chromium, in that order, all at pH 5.0. This was followed by a chromium solution at pH 2.5 and a mixed feed solution at pH 2.5. (Iron was omitted because of the precipitation of ferric oxide caused by the oxidation of the ferrous ion by the dichromate ion.) The analytical procedures including metal ion concentration, membrane thickness, conductivity, pH, and water flux are given in Appendix D. If it was suspected that the membranes had been damaged during the testing procedure, a final retest with the sodium chloride solution was made for comparison with the initial test. A schematic representation of one such test is shown in Figure 3.

Table 2. Reverse Osmosis Membranes Screened

A.	Commercial membranes
	1. Eastman asymmetric cellulose acetate, RO-97 (now RO-96)
	2. Eastman asymmetric cellulose acetate, RO-94 (no longer available)
	3. Eastman asymmetric cellulose acetate, RO-89 (replaced by RO-90)
	4. Amicon Diaflo ultrafiltration membrane, UM-10
	5. General Electric sulfonated polyphenylene oxide, JEPDM-127
B.	Membranes prepared from commercial polymers
	1. Ultrathin cellulose acetate, (Eastman 398-10)
	2. Ultrathin cellulose acetate, (Eastman 383-40)
	3. Ultrathin cellulose acetate, (Eastman 360-60)
	4. Ultrathin polyphenylene oxide, (General Electric)*†
	5. Ultrathin polycarbonate, (General Electric)*
	6. Ultrathin nylon, (Milvex 4000 -- General Mills)†
	7. Ultrathin cellulose ether, (Ethocel -- Dow)*
	8. Ultrathin cellulose acetate butyrate, (Eastman 171-15)
	9. Cross-linked asymmetric polyvinyl acetate, (#25-2813 National Starch and Chemical)*†
C.	Ultrathin membranes prepared from North Star polymers
	1. Cellulose acetate methyl sulfonate
	2. Methyl cellulose methyl sulfonate acetate
	3. β-glucan acetate dimethylaminoethyl ether
	4. Cellulose methyl sulfonate O-propyl sulfonic acid
	5. Cellulose acetate melamine formaldehyde adduct
	6. Methyl cellulose methyl sulfonate
	7. Gold, vacuum deposited on polysulfone

*Membranes cast from these polymers exhibited water fluxes of less than one gfd in preliminary tests with sodium chloride solutions.
†Membranes cast from these polymers exhibited rejections of less than ten percent in preliminary tests with sodium chloride solutions.

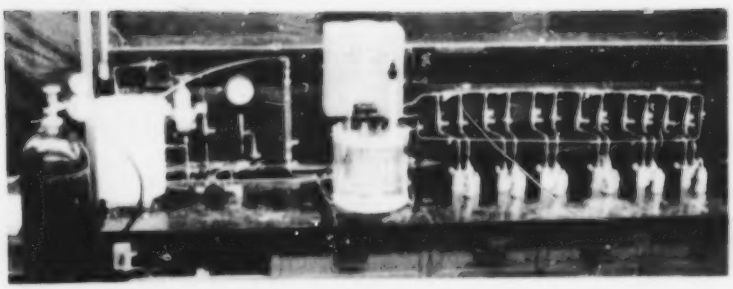

Figure 1. Reverse Osmosis Test System

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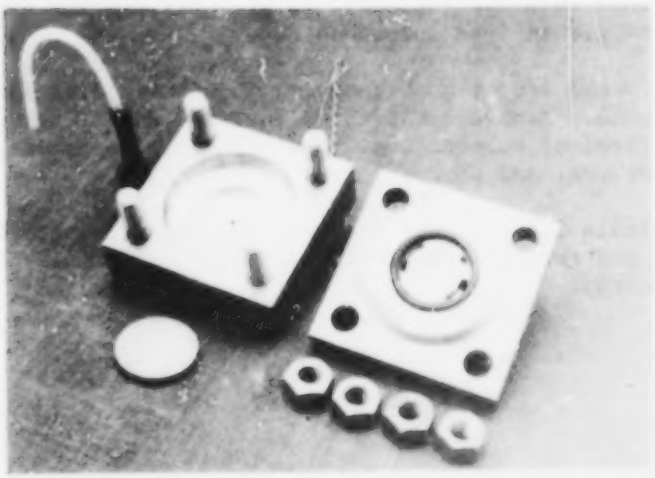

Figure 2. Reverse Osmosis Test Cell

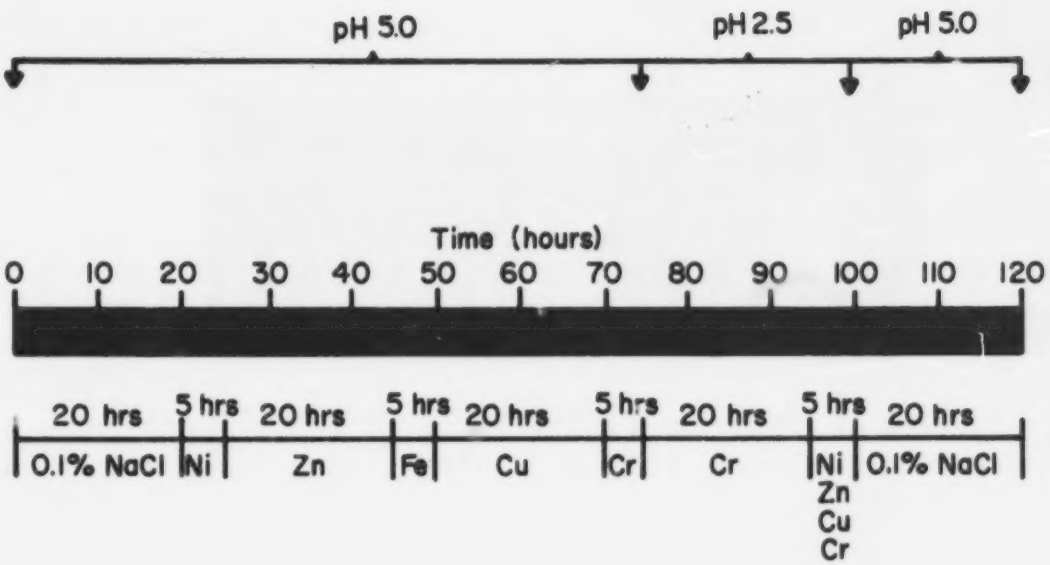

Figure 3. Schematic of a Typical Reverse Osmosis Test

Figure 4 shows a typical water flux curve for two cellulose acetate membranes during the testing procedure. After precompression, the water flux remained relatively steady (±1 gfd) through the entire test, despite changes in feed solutions.

Variables which would affect membrane performance were also investigated during this program. Membrane variables included annealing, membrane thickness, and chemical composition. Operating variables included temperature, pressure, and pH.

The outline in Table 3 summarizes the test conditions, analytical determinations, and reverse osmosis tests conducted during the first year of this program.

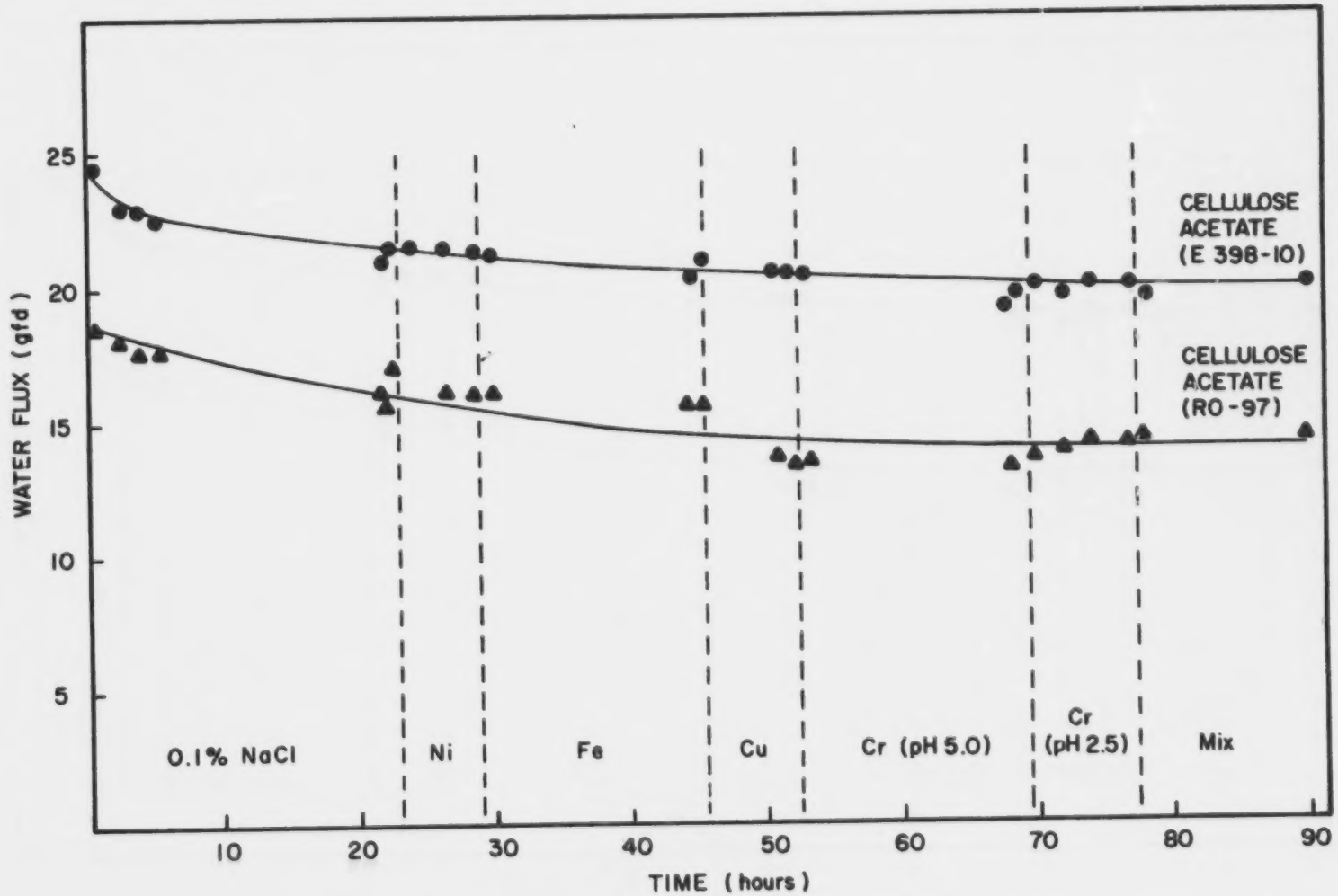

Figure 4. Typical Water Flux Behavior Across Membranes During Reverse Osmosis Treatment of Metal Ion Solutions

Table 3. Outline of Testing Program

I. Test Conditions
- A. Pressure . . . . . 600 psig
- B. Temperature . . . . . 25°C
- C. Feed flow . . . . . 1650 ml/min
- D. Test cell . . . . . flat plate

II. Analytical Procedures (Appendix D)
- A. Metal ion concentration -- atomic absorption
- B. Acid and base rejection -- pH measurement
- C. Cyanide ion concentration -- total carbon determination

III. Testing of Simulated Metal Finishing Waste Effluents
- A. Acidic rinses
  - 1. Metal ions
    - a. Ni^{++} (as sulfate)
    - b. Fe^{++} (as ammonium sulfate)
    - c. Cu^{++} (as sulfate)
    - d. Zn^{++} (as sulfate)
    - e. Cr^{+6} (as chromate ion)
  - 2. pH of metal ion solutions
    - a. 5.0 for Ni^{++}, Fe^{++}, Cu^{++}, and Zn^{++}
    - b. 5.0 and 2.5 for Cr^{+6}
  - 3. Determinations made on feed and product water
    - a. Water flux
    - b. Metal ion concentration
    - c. Acid concentration
- B. Basic copper cyanide rinses
  - 1. pH = ~ 11
  - 2. Determinations made on feed and product water
    - a. Water flux
    - b. Copper ion concentration
    - c. Cyanide concentration
- C. Acid- and base-containing solutions
  - 1. Acids and bases
    - a. Sulfuric acid
    - b. Hydrochloric acid
    - c. Nitric acid
    - d. Sodium hydroxide
  - 2. Determinations made on feed and/or product water
    - a. Water flux
    - b. Acid and base concentrations

IV. Variables affecting Membrane Performance
- A. Temperature
  - 1. 25° to 60°C
  - 2. Copper sulfate feed at pH 5.0
- B. Pressure
  - 1. 200 to 1000 psig
  - 2. Copper sulfate feed at pH 5.0
- C. pH
  - 1. 2.5 and 5.0
  - 2. Copper sulfate feed
- D. Membrane thickness

V. Optimization of Membrane System
- A. Chemical composition
- B. Annealing
- C. Thickness
- D. Membrane support

SECTION V

RESULTS

The results of the reverse osmosis tests are presented in six sections which are differentiated with respect to the type of wastewater or the performance variable being studied. These six sections are:

1) Acid wastewaters containing single metal salts

2) Acid wastewaters containing mixed metal salts

3) Alkaline copper cyanide bath rinse waters

4) Acids and bases

5) Test variables affecting membrane performance

6) Optimization of ultrathin membrane systems for better performance.

Acid Wastewaters Containing Single Metal Salts

Simulated wastewaters from plating baths containing nickel, iron, copper, zinc, and chromium ions were chosen for testing because they are the most commonly used and contain some of the more toxic metal ions. The metal ion concentration of these wastewaters is high enough to affect adversely the waterway into which it is discharged.

The evaluation of membranes for the removal of these individual species by reverse osmosis is presented in two separate sections. The first section presents the results obtained during evaluation of the nickel, iron, copper, and zinc wastewaters, and the second presents the results from tests with wastewaters containing chromic acid. The results are presented in these two sections because the chromic acid solutions behaved differently from the solutions containing the other metal ions.

Wastewaters Containing Nickel, Iron, Copper, and Zinc Salts

Short-term (< 20 hours) reverse osmosis tests were conducted on sixteen membranes using low concentration feed solutions containing approximately 100 mg per liter of the nickel, iron (ferrous), copper, or zinc ion (see Figure 3 for test procedure). Of these sixteen, six membranes that had shown either high rejections or high water fluxes were chosen for testing with an acidic copper sulfate solution which was concentrated from 500 to approximately 40,000 mg per liter of copper.

Low Concentration Feeds. Ultrathin membranes from three polymers showed the most promise in rejecting the nickel, iron, copper, and zinc ions at potentially high water flux. These three polymers were cellulose acetate

(E 360-60), β-glucan acetate dimethylaminoethyl ether (211-40A), and cellulose methyl sulfonate O-propyl sulfonic acid.

The results obtained for these membranes are presented in Table 4. Of these four, the cellulose acetate membrane exhibited the highest metal ion rejections (> 98 percent) with a good water flux of 30 gfd. The rejection of the β-glucan acetate dimethylaminoethyl ether was not quite as high (copper was the least rejected at 95.1 percent), but its water flux was an exceptional 47 gfd. Two different derivatives of the cellulose methyl sulfonate O-propyl sulfonic acid were tested. The 211-96B derivative had a high flux (42 gfd), but the rejections were lower than those of the other membranes. The 211-89A derivative, which contained a smaller amount of O-propyl sulfonic acid substituted on the cellulose unit than did the 211-96B derivative, exhibited a reduced water flux of 19 gfd, but gave a high rejection for each metal species (above 97 percent). It would be possible to vary the performance of the cellulose methyl sulfonate O-propyl sulfonic acid membrane by varying the amount of the substituents on the cellulose unit. A membrane could thus be synthesized to achieve a high rejection and a flux comparable to that of the other two membranes. (For a more complete explanation of the differences in reverse osmosis properties caused by chemical changes in the polymer properties, see the section on optimization of ultrathin membrane systems, page 49.) The water fluxes of the ultrathin membranes in Table 4 could be increased by casting them thinner.

Table 4. Reverse Osmosis Performance of Promising Membranes on Nickel, Iron, Zinc, and Copper Solutions

Test Conditions:

Temperature. . . . . 25°C
Pressure . . . . . 600 psig
Flow Rate. . . . . 1650 ml/min
Feed Metal Ion Concentration Range . . . . 100 ± 10 mg/liter
pH 5.0

Ultrathin Membrane	Thickness	Water Flux (gfd)		Metal Ion Rejection** (percent)			
		At 20 hrs	At 70 hrs	Ni	Fe	Cu	Zn
Cellulose Acetate (E 360-60)*	1200Å	35	30	>99.9	>99.9	>99.9	98.7
β-Glucan Acetate Dimethyl-aminoethyl Ether (211-40A)*	900Å	~47	~47	99.2	96.6	95.1	98.7
Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-96B)	1050Å	66	42	94.5	91.2	82.9	99.2
Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-89A)	1100Å	21	19	97.6	97.7	97.4	99.8

*pH 2.5.
**Calculated from measured values.

The choice of membrane for the treatment of wastewater containing the metal ions studied here would depend upon what flux was desired and what concentration of metal ion could be tolerated in the product water. If high rejection was necessary, the cellulose acetate membrane would be the choice. If high flux was desired and the rejection could be somewhat lower, the β-glucan acetate dimethylaminoethyl ether or the cellulose methyl sulfonate O-propyl sulfonic acid could be used.

To understand the data presented in Table 4 completely, three points must be explained.

1) The metal ion concentration is shown as 100 ± 10 mg per liter. This figure is given solely for the purpose of simplifying the table. This number indicates the *range* of concentrations measured in the feedwaters and not the *actual* concentrations. The rejection percentages were calculated from the actual measured (atomic absorption) values.

2) The water flux values are comparable because the membrane thicknesses were all approximately the same within the experimental error of ± 100 Å.

3) The pH of the feed solutions during the testing of the cellulose acetate (E 360-60) and β-glucan acetate dimethylaminoethyl ether was 2.5 rather than the 5.0 at which the other membranes were tested. This is because they were tested early in the program when 2.5 was the test pH. This changed to 5.0 to fall within the pH range for minimum membrane hydrolysis.[6]

Table 5 presents the reverse osmosis performance data for the other twelve membranes tested on the low-concentration wastewaters. The three points discussed above for Table 4 are also relevant for proper interpretation of Table 5.

Several membranes in Table 5 exhibited very high metal ion rejections. For example, the asymmetric membranes (>99.9 percent); ultrathin cellulose acetate, E 398-10 (>98.7 percent); cellulose acetate melamine formaldehyde adduct, 211-29B (>99.9 percent); and the methyl cellulose methyl sulfonate acetate, 211-64A (>99.2 percent). However, their water fluxes were not above 20 gfd. Two of the membranes, ultrathin cellulose acetate (E 398-10) and ultrathin cellulose acetate melamine formaldehyde adduct, could exhibit improved water fluxes if they were cast thinner. The ultrathin cellulose methyl sulfonate acetate could also be cast thinner, but its water flux would still be expected to be much lower than the desired 20 gfd. The water fluxes of the asymmetric membranes, of course, could not be improved. The Diaflo

Table 5. Reverse Osmosis Performance of Less-Promising Membranes on Nickel, Iron, Zinc, and Copper Solutions

Test Conditions:

Temperature . . . . . 25°C
Pressure. . . . . 600 psig
Flow Rate . . . . . 1650 ml/min
Feed Metal Ion Concentration Range. . . . . 100 ± 10 mg/liter
pH. 5.0

	Thickness	Water Flux (gfd)		Metal Ion Rejection (percent)*			
		At 20 hrs	At 70 hrs	Ni	Fe	Cu	Zn**
Asymmetric Cellulose Acetate (RO-97)	4 mils	17	14	>99.9	>99.9	>99.9	>99.9
Asymmetric Cellulose Acetate (RO-94)	4 mils	17	14	>99.9	>99.9	>99.9	--
Asymmetric Cellulose Acetate (RO-89)	4 mils	24	20	>99.9	>99.9	>99.9	--
Diaflo (UM-10)	--	66	43	54.8	45.4	48.3	72.4
Sulfonated Polyphenylene Oxide (JEPDM-127)	--	23	22	--	--	65.4	--
Ultrathin Cellulose Acetate (E 398-10)†	1000Å	20	18	>99.9	>99.9	>99.9	98.7
Ultrathin Cellulose Acetate (E 383-40)	1380Å	24	--	--	--	99.7	--
Ultrathin Cellulose Acetate Methyl Sulfonate (211-10C)†	1500Å	19	16	99.5	98.5	97.5	--
Ultrathin Cellulose Acetate Melamine Formaldehyde Adduct (211-29B)†	1050Å	21	18	>99.9	>99.9	>99.9	--
Ultrathin Methyl Cellulose Methyl Sulfonate Acetate (211-64A)†	1900Å	6	5	>99.9	>99.5	99.2	--
Ultrathin Cellulose Acetate Butyrate (EAB-171-15)	650Å	3	2	90.1	94.7	94.8	90.0
Ultrathin Gold on Polysulfone	~1000Å	5	4.5	53.0	50.5	36.8	69.7

*Calculated from measured values.
**Zn rejection was not determined for membranes tested early in the program.
†pH of 2.5.

The choice of membrane for the treatment of wastewater containing the metal ions studied here would depend upon what flux was desired and what concentration of metal ion could be tolerated in the product water. If high rejection was necessary, the cellulose acetate membrane would be the choice. If high flux was desired and the rejection could be somewhat lower, the β-glucan acetate dimethylaminoethyl ether or the cellulose methyl sulfonate O-propyl sulfonic acid could be used.

To understand the data presented in Table 4 completely, three points must be explained.

1) The metal ion concentration is shown as 100 ± 10 mg per liter. This figure is given solely for the purpose of simplifying the table. This number indicates the *range* of concentrations measured in the feedwaters and not the *actual* concentrations. The rejection percentages were calculated from the actual measured (atomic absorption) values.

2) The water flux values are comparable because the membrane thicknesses were all approximately the same within the experimental error of ± 100 Å.

3) The pH of the feed solutions during the testing of the cellulose acetate (E 360-60) and β-glucan acetate dimethylaminoethyl ether was 2.5 rather than the 5.0 at which the other membranes were tested. This is because they were tested early in the program when 2.5 was the test pH. This changed to 5.0 to fall within the pH range for minimum membrane hydrolysis.[6]

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ultrafiltration membrane exhibited a good water flux (42 gfd), but its rejection was much too low, as would be expected.

High-Concentration Feed. The importance of using membranes with high water fluxes and high rejections became apparent during a test in which an acidic copper sulfate feedwater (pH 5.0) was allowed to concentrate from 500 to approximately 40,000 mg per liter of copper. (In all other tests, the feed concentration was maintained at a constant value by recirculating the product water.) This test was conducted to simulate conditions which would be expected during the actual reverse osmosis treatment of a copper plating bath rinse water.

Six membranes chosen on the basis of their high flux-high rejection, or moderate flux-high rejection properties (see Table 5), were tested with this copper sulfate feed. These included:

1) Asymmetric cellulose acetate (RO-89)

2) Asymmetric cellulose acetate (RO-97)

3) Ultrathin cellulose acetate (E 398-10)

4) Ultrathin cellulose acetate (E 383-40)

5) Ultrathin cellulose acetate (E 360-60)

6) Cellulose methyl sulfonate O-propyl sulfonic acid (211-89A)

Since water flux was found to be inversely proportional to membrane thickness in the range 500 Å to 1500 Å (page 54), water fluxes at 1000 Å-thickness were calculated for the ultrathin membranes. This was done to facilitate the comparison of their reverse osmosis properties. (Rejection was not significantly affected by membrane thickness.)

Figure 5 shows these calculated water fluxes versus the copper concentration of the feedwater on semi-logarithmic plots for each of the six membranes. At a feed concentration of 2000 mg per liter copper, the water fluxes of all six membranes began an approximately linear decline to a concentration of 20,000 mg per liter copper. Between 20,000 and 40,000 mg per liter copper, the water fluxes declined more rapidly.

The decline in water flux with increasing copper concentration in the feedwater was attributed to two primary factors. The first factor was the increasing copper ion concentration of the feedwater, which caused an increase in the osmotic pressure. Table 6 gives the calculated osmotic pressures at the tested copper sulfate feed concentrations, and the method of calculation. As the osmotic pressure increased, the effective driving force (gage pressure minus osmotic pressure) decreased.

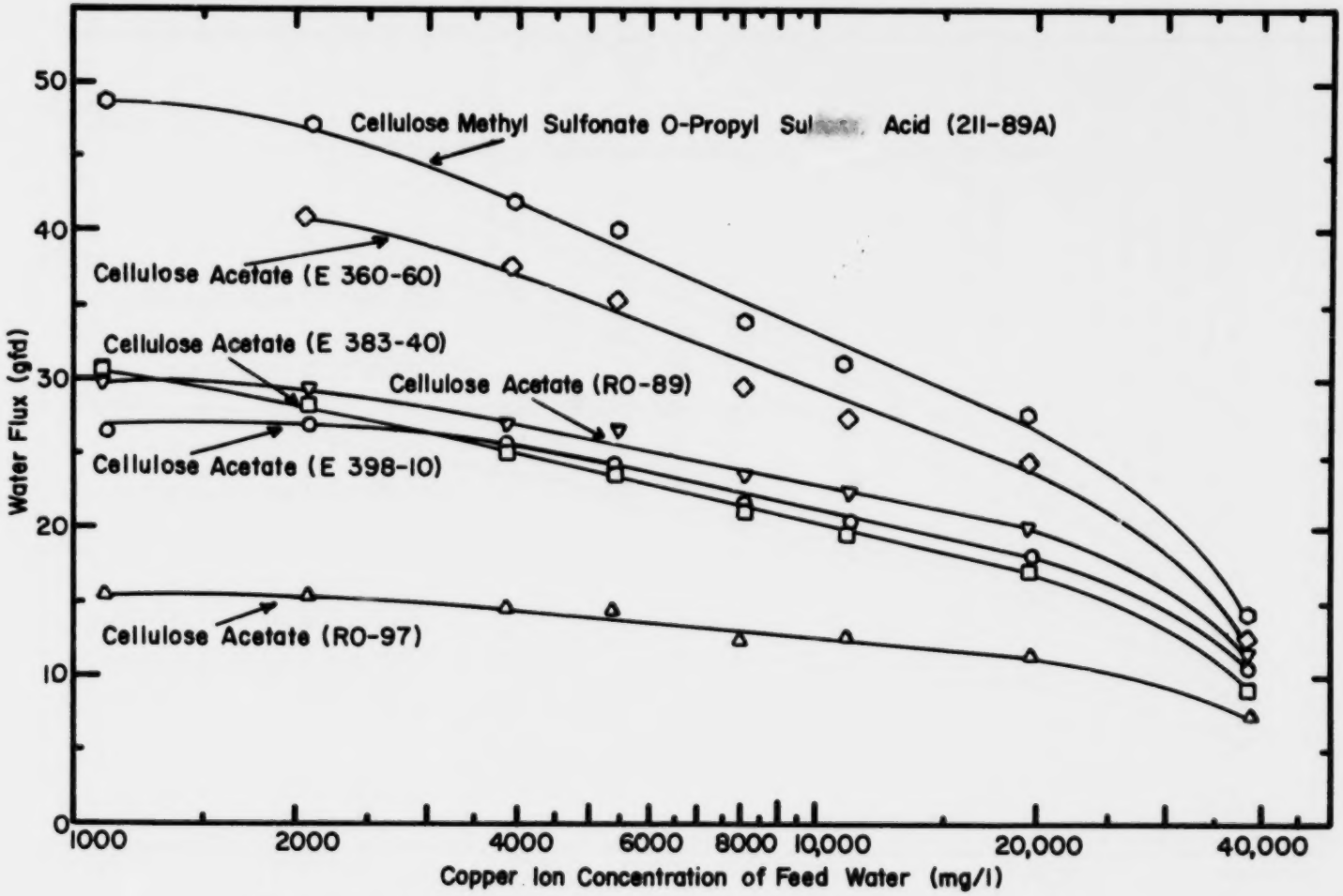


Figure 5. Effects of Increasing Feedwater Concentration on the Water Flux of Reverse Osmosis Membranes

Table 6. Osmotic Pressure and Effective Driving Force at Various Feedwater Concentrations

Concentration of Feedwater (mg/liter Cu)	Calculated* Osmotic Pressure (psi)	Effective Driving Force at 600 psig (gage pressure - osmotic pressure)
1,124	13	587
2,120	24	576
3,920	44	554
5,460	61	539
8,120	91	509
11,260	127	473
19,800	222	378
39,300	442	158

*Osmotic pressure $\Pi = 14.7\ cRT$

where:

c = molarity (mole l^{-1})

$R = 0.082$ (l-atm deg^{-1} $mole^{-1}$)

T = temperature (°K)

This caused a decrease in the water flux of the membrane since water flux varies directly with this effective driving force. Therefore, at a feedwater concentration of 20,000 mg per liter copper, the effective driving force was 378 psig instead of 600 psig. The increasing osmotic pressure was probably the primary cause of the decline in water flux in the linear portion (2000 to 20,000 mg per liter copper) of the curves in Figure 5.

The second factor which decreased the water flux was concentration polarization. The following is a brief description of concentration polarization.

> In reverse osmosis, the copper, salt, and water are brought to the membrane surface by convection. The water selectively passes through the membrane, leaving most of the copper salt at the membrane surface. Since the rate of transfer of the copper salt away from the membrane is diffusion controlled, an increase in the salt concentration at the membrane surface results (concentration polarization). This polarization causes an increase in the osmotic pressure at the membrane surface, which lowers the product water flux. Also, since the percentage salt rejection of the membrane is a constant (independent of salt concentration), the increase in the salt concentration near the membrane surface increases the salt gradient across the membrane and, in turn, increases the salt concentration in the product water. At a salt concentration of 100 mg per liter, a 90-percent-rejecting membrane would give product water containing ten ppm salt. At a salt concentration of 500 mg per liter, the same membrane would give product water containing 50 ppm. Thus, concentration polarization causes a lower water flux and an apparent lower salt rejection.

Concentration polarization not only can cause a decrease in flux, but also can result in a lower salt rejection. The more rapid water flux decline in Figure 5 between feedwater concentrations of 20,000 and 40,000 mg per liter copper was probably caused by concentration polarization. This was evidenced by the fact that the high-flux membranes exhibited a sharper drop in flux than did the low-flux membranes. These sharper flux decreases of the high-flux membranes were attributed to greater concentration of polarization effects caused, in turn, by a relatively faster buildup of copper sulfate at membrane surfaces. It should also be noted that as the copper concentration of the feedwater increased, the difference in water flux between the lowest- and highest-flux membranes steadily decreased. In Figure 5, at 1000 mg per liter copper, water fluxes of the membranes varied from 15 to 49 gfd--a 34 gfd difference. At 40,000 mg per liter copper, they ranged from 9 to 15 gfd--a 6 gfd difference.

Figure 6 shows the curves of the copper concentration of the product water versus that of the feedwater for each membrane (semi-logarithmic plot). The copper rejection for all six membranes was greater than 99 percent at all feed concentrations tested. It was evident, and to be expected, that as the feedwater concentration increased, the product water concentration increased.

Of the three polymers giving the best reverse osmosis performance using feedwaters at approximately 100 mg per liter of metal ions (Table 4), two were tested with the high-copper-containing feed; cellulose acetate (E 360-60) and a cellulose methyl sulfonate O-propyl sulfonic acid (211-89A). Although complete data were not available on the performance of the β-glucan acetate dimethylaminoethyl ether at all the copper feed concentrations investigated during this test, this membrane exhibited a corrected water flux of 34 gfd and a 99.8-percent rejection of copper ions when tested on a 5220 mg per liter copper (as sulfate) feed solution. This water flux is only slightly below that of the cellulose acetate (E 360-60), when tested on a feed of similar copper concentration (see Figure 5). Assuming that the behavior of the β-glucan acetate dimethylaminoethyl ether corresponded to that of the other membranes tested, it would appear to be the third best performing membrane. Here again then, as in the tests with feeds containing lower metal ion concentrations, the three best performing polymers were ultrathin cellulose acetate (E 360-60), a cellulose methyl sulfonate O-propyl sulfonic acid derivative, and β-glucan acetate dimethylaminoethyl ether.

Pressure Effects. It was stated previously that, as the copper concentration in the feedwater increased, the osmotic pressure increased, thus reducing the effective driving force. It would therefore be expected that by increasing the pressure from 600 to 1000 psig, the water flux and copper rejection of the membranes could be improved.

Table 7 gives the water fluxes and the copper ion concentration of the product water at 600 psig and 1000 psig. The feedwater concentrations were 39,000 mg per liter copper and 43,000 mg per liter copper, respectively. Increasing the pressure increased the water flux and decreased the copper ion concentration of the product water. This latter effect occurred because the flow of water through the membrane is pressure-dependent, in contrast to the passage of the copper salt through the membrane which is diffusion-dependent; *i.e.*, the diffusion of copper ion through the membrane remains constant while the flow of water through the membrane increases with an increase in pressure.

This results in an effective decrease in the copper concentration of the product water.

Conclusions and Discussion. Ultrathin membranes from three polymers, cellulose acetate (E 360-60), cellulose methyl sulfonate O-propyl sulfonic acid, and β-glucan acetate dimethylaminoethyl ether, have shown water fluxes and metal ion rejections superior to all other membranes tested by reverse osmosis on feedwaters containing metal

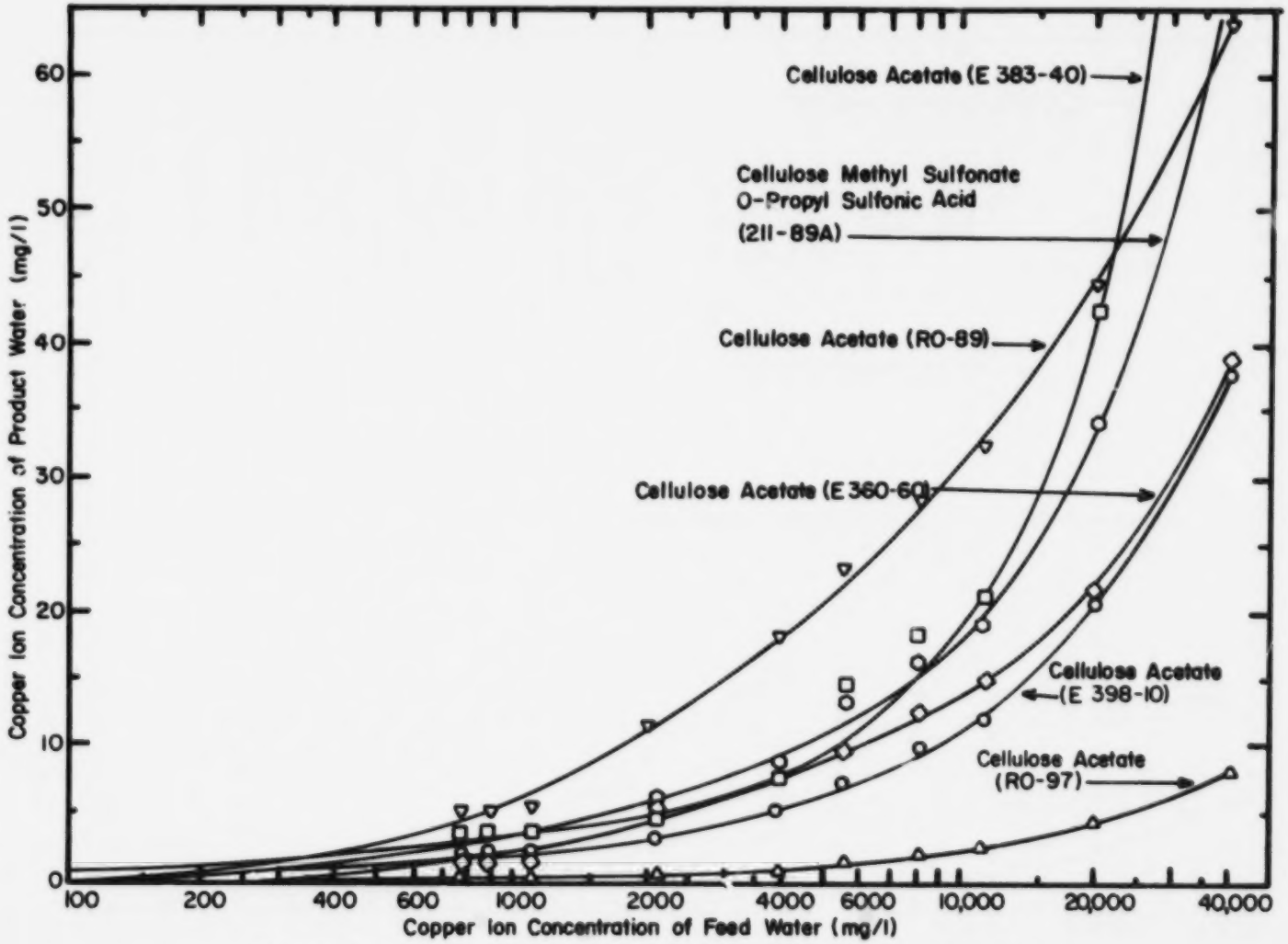


Figure 6. Effects of Increasing Feedwater Concentration on the Copper Ion Concentration of the Product Water

Table 7. Water Fluxes and Copper Ion Concentrations Obtained at Pressures of 600 and 1000 psig

Test Conditions:

Temperature . . . . . 25°C
Flow Rate . . . . . 1650 ml/min

Membrane	Water Flux (gfd)*		Copper Concentration of Product Water	
	600 psig	1000 psig	600 psig (39,300 mg/l Cu^{++} feed)	1000 psig (43,400 mg/l Cu^{++} feed)
Ultrathin Cellulose Acetate (E 398-10)	10.8	18.4	38.0	15.5
Ultrathin Cellulose Acetate (E 383-40)	9.2	14.5	104.6	48.5
Ultrathin Cellulose Acetate (E 360-60)	13.1	20.2	43.6	33.7
Asymmetric Cellulose Acetate (RO-97)	7.3	13.0	8.4	4.8
Asymmetric Cellulose Acetate (RO-89)	11.1	16.7	64.2	27.2
Ultrathin Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-89A)	15.0	25.4	71.8	41.0

*Water fluxes are corrected to 1000 Å for the ultrathin membranes.

ions. Also, treatment of metal finishing wastewaters containing copper sulfate by these same membranes in a reverse osmosis system operating at a pressure of 600 psig, limits the practical concentration of the copper sulfate solution to between 20,000 and 40,000 mg per liter copper. This concentration is approximately forty to eighty percent of the copper concentration of a general acid copper plating bath (51,500 mg per liter copper). By operating the system at higher pressures, it should be possible to obtain a concentration closer to 100 percent bath concentration, while maintaining good flux and relatively low copper ion concentrations in the product water.

The effects of concentration polarization could also be minimized by proper design of the reverse osmosis cells (or tubes) and the use of turbulence promoters. Reduction of these effects would result in 1) product waters containing lower copper concentrations, and 2) increased water fluxes caused by the reduction of osmotic pressure differences at the membrane surface (caused by the buildup of salts). Such improvements would also enable the reverse osmosis system to concentrate the feedwaters to a greater degree than was obtained in the above test.

Wastewaters Containing Chromic Acid

Chromic acid was observed to behave differently from the other metal species. Short-term tests (<20 hours) of sixteen membranes were conducted at pH 5.0 and 2.5 (Figure 3) using low concentration feedwaters containing approximately 100 mg per liter of chromium. These two pH's were chosen because pH 2.5 is the pH of a 100 mg per liter chromic acid (as chromium) solution, and pH 5.0 is the pH at which minimum hydrolysis of cellulose acetate membranes occurs.[6]

With the knowledge that chromic acid is a powerful oxidizing agent and that the pH of 2.5 of a 100 mg per liter chromium solution would eventually cause membrane hydrolysis, it was decided to run additional tests of longer duration in order to observe any effects these two phenomena would have on membrane performance.

Short-Term Testing. Table 8 gives the short-term test results for the seven best membranes of the sixteen tested. These seven were chosen on the basis of their moderate to high water fluxes and their adequate to good chromium rejections at pH 5.0. Examination of the rejections indicated that chromic acid was generally more difficult to reject than were the other metal salts. For example, ultrathin cellulose acetate (E 360-60) rejected only 75.0 percent of the chromium (at pH 5.0) and >98 percent of the nickel, iron, copper, and zinc ions (Table 4).

It was also observed that chromic acid was rejected better if the solution was at pH 5.0, rather than 2.5. This improved rejection could be caused by a shift in the chromate-dichromate equilibrium. The lower acidity at pH 5.0 would cause a decrease in the concentration

Table 8. Reverse Osmosis Performance of Membranes on Chromic Acid Solutions

Test Conditions:

Temperature . . . . . 25°C
Pressure. . . . . 600 psig
Flow Rate . . . . . 1650 ml/min
Chromium Concentration Range. . . . 100 ± 10 mg/liter

Membrane	Thickness	Water Flux (gfd) at 70 hours	Chromium Rejection (percent)*	
			pH 2.5	pH 5.0
Ultrathin Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-89A)	1100 Å	19	90.8	96.5
Ultrathin Cellulose Acetate Melamine Formaldehyde Adduct (211-29B)	1050 Å	18	83.3	--
Ultrathin Cellulose Acetate (E 398-10)	1000 Å	18	88.3	94.1
Ultrathin Cellulose Acetate (E 360-60)	1200 Å	30	47.8	75.0
Asymmetric Cellulose Acetate (RO-97)	4 mils	14	90.0	98.3
Asymmetric Cellulose Acetate (RO-89)	4 mils	20	85.1	92.2
Sulfonated Polyphenylene Oxide (JEPDM-127)	0.2 mil	23	56.5	79.5

*Calculated from measured values.

of the dichromate ion, which may be difficult to reject, and a corresponding increase in the concentration of the chromate ion, which may be easier to reject. The testing of this hypothesis, however, was not within the scope of this program.

Of the sixteen membranes tested, only one exhibited any change in water flux with chromium, compared to that obtained with other metal ions. That membrane was β-glucan acetate dimethylaminoethyl ether. During tests on solutions containing nickel, iron, copper, and zinc salts, this membrane (900Å) exhibited a water flux of ∿47 gfd at pH 2.5. However, when the feed solution was changed to the chromic acid at pH 2.5, the water flux dropped to 29 gfd.

Long-Term Tests. To determine what effects longer exposure to chromic acid would have on membrane performance, three of the seven membranes listed in Table 8 were selected for further testing. These three membranes, chosen because of their high chromium rejections, were asymmetric cellulose acetate (RO-97), ultrathin cellulose acetate (E 398-10), and ultrathin cellulose methyl sulfonate O-propyl sulfonic acid (211-89A). The two ultrathin membranes exhibited similar water fluxes at the same thickness.

The three membranes were exposed to chromic acid feedwaters (100 mg per liter chromium) for a total of 170 hours: 140 hours at pH 2.5, followed by 30 hours at pH 5.0. Table 9 gives the results of the reverse osmosis tests. A decrease in the chromium rejection for all three membranes was observed in tests made at 65 and 140 hours at pH 2.5. A test of the membranes with a copper sulfate solution at 140 hours (pH 2.5) showed no evident degradation of the membranes attributable to either oxidation or hydrolysis. Therefore, no satisfactory explanation for this decline can be given at this time. It is expected, however, that the membranes would show definite effects of oxidation or hydrolysis during longer exposure to chromic acid feed solutions at pH 2.5.

An improvement in the rejection of the chromic acid with a change in pH from 2.5 to 5.0 was again observed. The change in pH was not only advantageous for better chromium rejection, but it also was advantageous because at pH 5.0 the oxidizing power of the dichromate ion is lessened and hydrolysis of the cellulose acetate is minimal.[6] A major disadvantage to changing the pH is the need to add a neutralizing base to the solution to maintain the pH at 5.0.

Conclusions and Discussion. On the basis of water flux and rejection, three membranes appear to be best in treating chromic acid solutions. These are ultrathin cellulose methyl sulfonate O-propyl sulfonic acid (211-89A), ultrathin cellulose acetate (E 398-10), and asymmetric cellulose acetate (RO-97). The asymmetric cellulose acetate membrane (RO-97) and the ultrathin cellulose methyl sulfonate O-propyl sulfonic

Table 9. Reverse Osmosis Performance of Three Promising Membranes on Chromic Acid Solutions

Test Conditions:

Temperature . . . . . 25°C
Pressure. . . . . 600 psig
Flow Rate . . . . . 1650 ml/min
Chromium Concentration Range. . . 95 ± 1 mg/liter

Membrane	Membrane Thickness	Water Flux Through Membrane (gfd)			Percent Rejection of Cr^{+6} in Product Water*		
					pH 2.5		pH 5.0
		65 hrs	140 hrs	170 hrs	65 hrs	140 hrs	170 hrs
Asymmetric Cellulose Acetate (RO-97)	4 mils	17	18	17	93.8	89.6	97.8
Ultrathin Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-89A)	530 Å	25	27	28	95.4	90.0	97.4
Ultrathin Cellulose Acetate (E 398-10)	1200 Å	17	18	18	84.8	82.8	90.0

*Calculated from measured values.

acid exhibited similar rejections at pH 5.0. However, the latter membrane exhibited the higher water flux of the two. In addition, because of its ultrathin nature, the water flux of the ultrathin cellulose methyl sulfonate O-propyl sulfonic acid membrane could further be improved by casting it thinner. Such an improvement is evident by comparing the flux of this membrane in Tables 8 and 9; a 530-Å-thick membrane exhibited a water flux of 25 gfd compared to the 19 gfd exhibited by a 1000-Å-thick membrane.

Of these three membranes only one, cellulose methyl sulfonate O-propyl sulfonic acid (211-89A), was among the four membranes found most effective for treating the metal salt solutions, and this membrane was the least effective of the four (lowest flux). This indicates that one membrane cannot be used for the successful treatment of a variety of waste effluents; *i.e.*, the membrane which can most effectively treat a chromic acid waste solution is not necessarily the one which can most effectively treat a copper sulfate waste solution.

It is evident from the above results that there are two possible approaches to the reverse osmosis treatment of rinses containing chromic acid. The first approach is to use a membrane that is resistant to acid hydrolysis and oxidation and has a high chromic acid rejection at low pH. Of the membranes tested, only the cellulose methyl sulfonate O-propyl sulfonic acid membrane (211-89A) has been shown to be somewhat more acid (and base) resistant to hydrolysis than cellulose acetate membranes. This resistance was caused by the substituted methyl sulfonate and ether groups, which are less susceptible to acid and base hydrolysis than are acetate groups. However, the resistance of this membrane to chromic acid oxidation during long-term testing at pH 2.5 or lower has not yet been determined.

The second approach to the problem is adjusting the pH of the solution to 5.0. At pH 5.0, membrane hydrolysis (and possibly oxidation) would be minimal so that any one of the three high-rejecting membranes shown in Table 9 could be used in the treatment of chromic acid wastewaters. Such an approach would be possible, however, only if the chromium were to be discarded or reclaimed by another method, since the addition of the neutralizing base would contaminate the concentrate, making it unfit for reuse. If neutralization to pH 5.0 were the approach taken, waste solutions from alkaline cleaning or stripping baths could be used in the neutralization process.

Acid Wastewaters Containing Mixed Metal Salts

In addition to single metal salt solutions, mixed feedwaters containing approximately 100 mg per liter of nickel, copper, zinc, and chromium were also subjected to reverse osmosis. Iron was excluded from these mixtures because the ferrous ion was quickly oxidized to the ferric ion by the dichromate and then precipitated as iron oxide. The pH of these solutions was 2.5, because of the chromic acid content.

Table 10 compares the rejections obtained during tests using solutions containing single metal salts and those using a mixture of salts. The five membranes chosen for comparison were those found to be the most promising for treating the various single metal rinse waters, as discussed in the previous section. In almost all of these tests the differences in rejection values were less than two percent. This difference was not considered significant.

Only one of these membranes exhibited water flux changes when the feed solutions were changed from single salt to mixed salt feedwaters. That was β-glucan acetate dimethylaminoethyl ether. As indicated previously, this membrane dropped in flux from 47 to 29 gfd when switched from a copper solution to a chromic acid solution. When this membrane was then switched to a mixed feed solution, the flux returned to 47 gfd. It is significant that there was no chromic acid in this particular mixed feed solution, which would indicate that this membrane was sensitive to the presence of chromic acid.

Alkaline Copper Cyanide Bath Rinse Waters

In addition to the acidic electroplating solutions which have just been discussed, the metal finishing industry uses alkaline plating baths which consist mainly of heavy metal cyanide complexes and free cyanide salts. Because these complex cyanides are extremely toxic to aquatic life, they must be removed from the waste rinse waters prior to discharge into the environment.

Alkaline Hydrolysis of Membranes

Before reverse osmosis tests with a metal cyanide solution could be undertaken, at least one membrane had to be found which could withstand the alkaline hydrolysis at the high pH's of the metal cyanide rinse solutions. Several membranes which had been precompressed were therefore tested for 48 hours with a one-tenth-percent sodium chloride solution at pH 11. Table 11 gives the water fluxes and conductivity rejections of four representative membranes.

It was evident from this test that the only membrane to withstand the alkaline conditions was the sulfonated polyphenylene oxide (General Electric JEPDM-127). The water flux and rejection remained

Table 10. Metal Ion Rejections from Reverse Osmosis Tests on Membranes with Feedwaters Containing Single Metal Salts and with Those Containing Mixed Metal Salts

Test Conditions:
Temperature . . . . . 25°C
Pressure. . . . . 600 psig
Flow Rate . . . . . 1650 ml/min

Membrane	Single Metal Ion Feedwater				Mixed Metal* Ion Feedwater			
	Ni	Zn	Cu	Cr**	Ni	Zn	Cu	Cr**
Ultrathin Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-89A)	97.6	99.8	97.4	90.8	98.4	96.8	98.3	92.2
Ultrathin Cellulose Acetate (E 360-60)	>99.9	98.4	>99.9	31.3	>99.9	96.6	>99.9	30.8
Ultrathin Cellulose Acetate (E 398-10)	>99.9	98.7	>99.9	88.3	>99.9	--	99.9	86.3
Ultrathin ß-glucan Acetate Dimethylaminoethyl Ether (211-40A)	99.2	98.7	95.1	26.3	97.7	--	97.3	--
Asymmetric Cellulose Acetate (RO-97)	>99.9	>99.9	>99.9	90.0	>99.9	--	>99.9	93.8

*Some of the early tests did not include zinc or chromium
**At pH 2.5.

Table 11. Reverse Osmosis Performance of Precompressed Reverse Osmosis Membranes under Alkaline Conditions

Test Conditions:

Temperature . . . . . 25°C
Pressure. . . . . 600 psig
Flow Rate . . . . . 1650 ml/min
Feed. . . . . 0.1-percent NaCl at pH 11.0 to 11.5
Time of Test. . . . . 48 hours

Membrane	Water Flux Through the Membrane (gfd)		Percent Rejection Based on Conductivity	
	Initial	After 48 hours	Initial	After 48 hours
Asymmetric Cellulose Acetate (RO-97)	15	9	94	9
Ultrathin Cellulose Acetate (E 398-10)	19	40	90	22
Ultrathin Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-89A)	18	31	96	86
Sulfonated Polyphenylene Oxide (JEPDM-127)	23	22	51	52

essentially constant during the entire test (low sodium chloride rejection is a property of this membrane). The only other membrane to exhibit any resistance was a cellulose methyl sulfonate O-propyl sulfonic acid derivative (211-89A), which had a large flux change, but a relatively small decrease in rejection. The cellulose acetate membranes were rapidly degraded by the alkaline conditions and were obviously not candidates for treating high pH feedwaters.

Tests with Copper Cyanide Feed

From the above, it was decided to evaluate polyphenylene oxide and the sulfonated cellulose methyl sulfonate O-propyl sulfonic acid (211-89A) membranes on a simulated copper cyanide rinse water, with asymmetric cellulose acetate (RO-97) as a control.

The testing was divided into five phases in a total test period of 95 hours. The three membranes were precompressed for 18 hours with a one-tenth-percent solution of sodium chloride (first phase). They were then tested on a feed which was approximately a 1:100 dilution of a standard alkaline copper plating bath containing 26 g per liter cuprous cyanide, 44 g per liter sodium cyanide, and 3.7 g per liter sodium hydroxide (second phase).[7] The pH of the 1:100 dilution was 10.4. After testing the membranes for 49 hours on the 1:100 dilution at pH 10.4, the pH was changed to 11.4 by the addition of sodium hydroxide. The membranes were then tested for 24 hours at this higher pH to determine the effects of a higher alkaline concentration on the performance of the membranes (third phase). This higher concentration of sodium hydroxide would have the effect of accelerating the alkaline hydrolysis of the membranes, giving a faster indication of their ability to withstand degradation. The testing using the two 1:100 diluted feeds was followed by two shorter tests. The first of these (fourth phase) was conducted on a 1:10 dilution of the plating bath (pH 11.4) to determine the rejection at higher solute concentrations. The final test (fifth phase) was conducted using a one-tenth-percent sodium chloride feed solution. Significant flux increases coupled with rejection decreases would indicate if the membranes had been degraded during the testing procedure.

In Figure 7, the water fluxes of each membrane during the first three phases of the test are plotted versus time. All three membranes exhibited an initial flux decline due to membrane compaction. When the feed was changed from the sodium chloride solution to the 1:100 bath dilution at pH 10.4 (from first to second phase), the sulfonated polyphenylene oxide and the cellulose methyl sulfonate O-propyl sulfonic acid exhibited an initial increase in water flux which was attributed to membrane swelling caused by the alkaline conditions.

After this initial flux increase in the second phase, the sulfonated polyphenylene oxide exhibited the expected compressive flux decline, while the cellulose methyl sulfonate O-propyl sulfonic acid and the

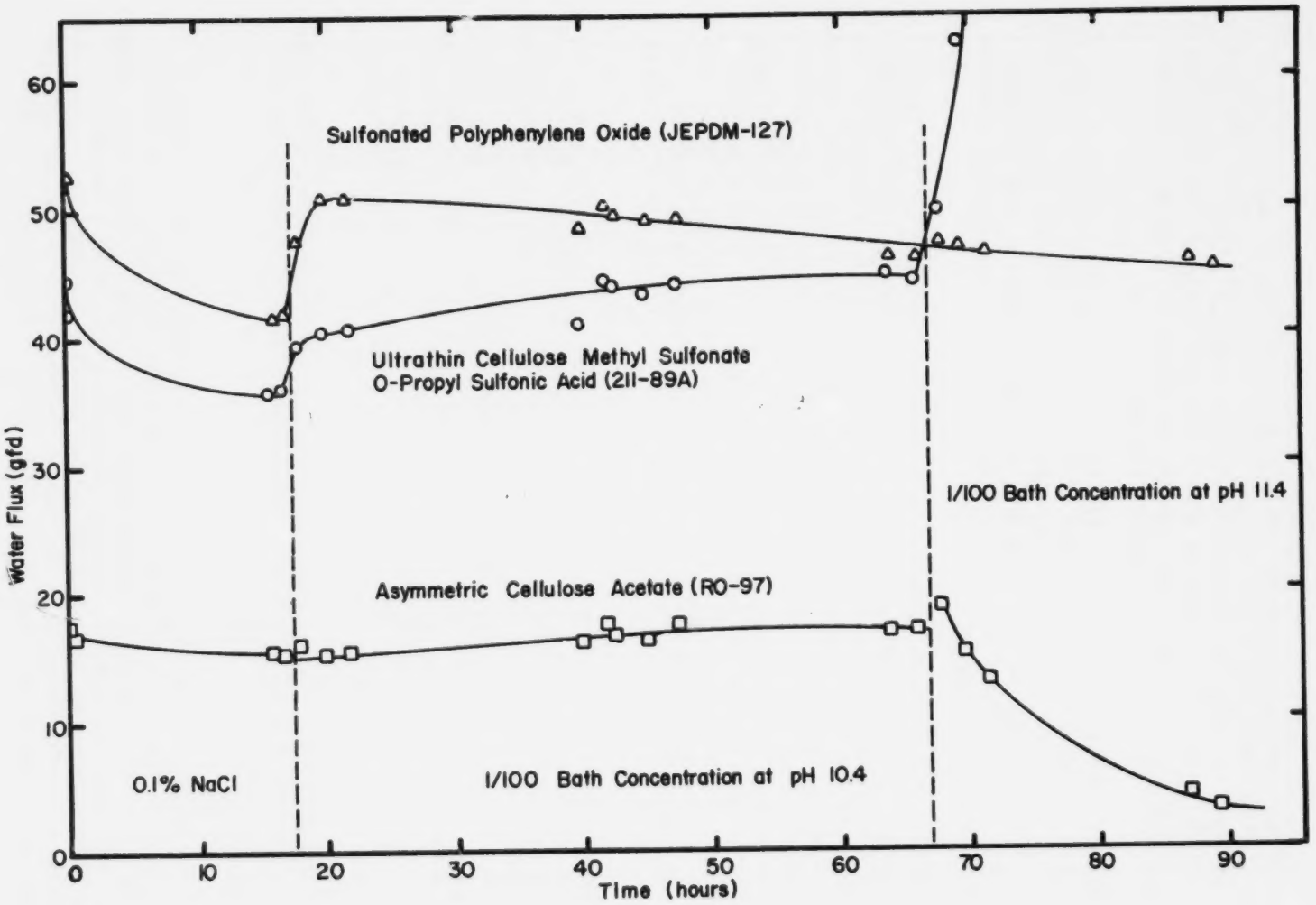


Figure 7. Water Flux Behavior During Reverse Osmosis Treatment of Copper Cyanide Rinse Waters

cellulose acetate both exhibited a gradual increase in water flux during the remainder of the testing phase. Although such an increase in water flux might be indicative of some membrane degradation, this evidence alone was regarded as insufficient to conclude any degradation had occurred. No significant changes in copper or cyanide rejection were observed during this phase of the test.

When the pH was raised to 11.4 (third phase), however, definite flux changes were evident. The water flux of the cellulose methyl sulfonate O-propyl sulfonic acid increased rapidly, and that of the asymmetric cellulose acetate (RO-97) decreased (probably caused by the collapse of the porous substrate). The sulfonated polyphenylene oxide membrane exhibited no apparent change in water flux.

Tables 12 and 13 give the copper and cyanide rejections of all three membranes for the first three phases of testing using copper cyanide feed solutions. For both the cellulose methyl sulfonate O-propyl sulfonic acid and the cellulose acetate (RO-97) membranes, the copper and cyanide rejections decreased when the pH of the feed solution was increased from 10.4 to 11.4. For the cellulose methyl sulfonate O-propyl sulfonic acid, the copper rejection dropped from 99.7 to 56.2 percent and the cyanide rejection dropped from 95.8 to 49.3 percent. The cellulose acetate (RO-97) exhibited smaller increases of 98.1- to 75.9-percent rejection for cyanide. The sulfonated polyphenylene oxide membrane exhibited no change in the rejection of either of these two solute species.

From the above data it appeared that the sulfonated polyphenylene oxide was the only membrane to withstand hydrolysis by the highly alkaline feed solutions. This membrane would therefore be the only one for which solute rejections at a higher feed concentration could be quantitatively determined (although others are given). The test with a feed at a 1:10 dilution of the plating bath (pH 11.4) showed a decrease of about three percent in the copper rejection (98.5 to 95.4 percent) and a similar decrease of about two percent in the cyanide rejection (93.0 to 90.9 percent). This decrease in rejection was most probably caused by concentration polarization.

A final test with a one-tenth-percent sodium chloride solution was made to determine to what extent the membranes had deteriorated during the testing procedure. Table 14 gives the initial and the final salt rejections for the three membranes.

The large decrease in the salt rejections of the cellulose methyl sulfonate O-propyl sulfonic acid and the cellulose acetate (RO-97) membranes indicated (and substantiated earlier observations) that these two membranes had been extensively damaged in the pH 11.4 solution. The sodium chloride rejection of the sulfonated polyphenylene oxide membrane, on the other hand, increased substantially. Such an increase could be caused by membrane compaction and the deposition of solid

Table 12. Rejection of Copper During Reverse Osmosis Treatment of a Copper Cyanide Waste Solution

Test Conditions:

Temperature . . . . . 25°C
Pressure. . . . . 600 psig
Flow Rate . . . . . 1650 ml/min
pH. . . . . 10.4 and 11.4
Feed. . . . . 1/100 bath concentration -- 218 ± 2ppm Cu
1/10 bath concentration -- 2400 ± 15 ppm Cu
Time of Tests . . . . . 50 hours on 1/100 bath concentration
23 hours on 1/10 bath concentration

Membrane	Percent Copper Rejection			Copper in Product Water (mg/l)		
	1/100 bath conc.		1/10 bath conc.	1/100 bath conc.		1/10 bath conc.
	pH 10.4	pH 11.4	pH 11.4	pH 10.4	pH 11.4	pH 11.4
Sulfonated Polyphenylene Oxide (JEPDM-127)	98.7	98.5	95.4	2.8 ± 0.5	3.2 ± 0.5	110 ± 1
Ultrathin Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-89A)	99.7	56.2	44.5	0.58 ± 0.05	95.6 ± 1.0	1330 ± 15
Asymmetric Cellulose Acetate (RO-97)	98.1	75.9	59.7	4.06 ± 0.04	52.6 ± 0.5	968 ± 15

Table 13. Rejection of Cyanide During Reverse Osmosis Treatment of a Copper Cyanide* Waste Solution

Test Conditions:

Temperature . . . . . 25°C
Pressure. . . . . 600 psig
Flow Rate . . . . . 1650 ml/min
pH. . . . . 10.4 and 11.4
Feed. . . . . 1/100 bath concentration -- approximately 325 ± 4 mg/l of Carbon
1/10 bath concentration -- 2905 ± 50 mg/l of Carbon
Time of Test. . . . . 50 hours on 1/100 bath concentration
23 hours on 1/10 bath concentration

Membrane	Percent Rejection of Cyanide			Total Carbon in Product Water (mg/l)		
	1/100 bath conc.		1/10 bath conc.	1/100 bath conc.		1/10 bath conc.
	pH 10.4	pH 11.4	pH 11.4	pH 10.4	pH 11.4	pH 11.4
Sulfonated Polyphenylene Oxide (JEPDM-127)	93.3	93.0	90.9	20.1 ± 0.5	24.8 ± 0.5	256 ± 4
Ultrathin Methyl Sulfonate O-Propyl Sulfonic Acid (211-89A)	95.8	49.3	33.3	12.8 ± 0.5	180 ± 4	1940 ± 50
Asymmetric Cellulose Acetate (RO-97)	94.5	64.8	48.1	16.8 ± 0.5	125 ± 4	1515 ± 50

*Cyanide was determined using a Beckman Total Organic Carbon Analyzer (TOC). Results are reported as mg/l of carbon. To convert to mg/l cyanide, multiply by 2.17.

Table 14. Initial and Final Rejections of 0.1-Percent NaCl Solutions to Determine Membrane Deterioration

Membrane	NaCl Rejections (percent)	
	Initial	Final
Sulfonated polyphenylene oxide	71.2	84.8
Ultrathin cellulose methyl sulfonate O-propyl sulfonic acid (211-89A)	91.4	19.6
Asymmetric cellulose acetate (RO-97)	96.3	0

oxidation products on the membrane. Thus, the membrane had not been damaged. The water flux of the sulfonated polyphenylene oxide membrane after 95 hours of testing was 45 gfd.

Conclusions

Three conclusions may be drawn from the above data.

1) The sulfonated polyphenylene oxide membrane is an excellent candidate for treating alkaline cyanide waste solutions. Under acid conditions this membrane exhibited low rejections toward metal ions (Tables 5 and 8). Under alkaline conditions it exhibited:

   a) No changes in water flux or copper and cyanide rejection when the pH was increased from 10.4 to 11.4 (*i.e.*, no hydrolysis);

   b) An increase in the sodium chloride rejection over the entire test time;

   c) A water flux of 45 gfd after 95 hours of testing; and

   d) High rejection of the solvent species (98.5 percent for copper and 93 percent for cyanide).

2) The cellulose methyl sulfonate O-propyl sulfonic acid cannot be used for the reverse osmosis treatment of alkaline cyanide waste solutions. The rapid increase in water flux at pH 11.4, the decreased copper and cyanide rejections at

pH 11.4, and the decreased salt rejection indicate that the membrane was very susceptible to alkaline hydrolysis.

3) Concentration polarization is probably responsible for small decreases in the copper and cyanide rejections of the sulfonated polyphenylene oxide membrane when the feed concentration is increased by a factor of ten. This problem could be lessened by the introduction of turbulence promoters into the reverse osmosis system.

Acids and Bases

Most metal finishing operations use acid or alkaline cleaning solutions to remove stains and surface contaminants. These solutions most often contain sulfuric, hydrochloric, or nitric acids or sodium hydroxide. These acids and the base are also found in stripping solutions which are used to refinish previously plated work, to rework damaged plating, and to remove undesirable metallic or inorganic surface coatings.

Reverse osmosis tests were conducted to determine the general extent to which each of the above acidic or basic species was rejected by promising membranes for treating wastes containing metal ions. The test procedure included precompressing the membranes for over twenty hours with a solution containing zinc sulfate and sulfuric acid, to determine the effect of a metal salt on acid rejection, and then testing them on each individual acid and base for a period of one hour. The order of testing was sulfuric, hydrochloric, and nitric acids followed by sodium hydroxide. Table 15 gives the membranes and their rejections for each acidic or basic species.

Several conclusions can be drawn from the data in Table 15.

1. Sulfuric acid was rejected better from a solution containing a metal ion -- in this case, zinc -- than from a solution which contained only the acid.

2. The order of rejection of the acidic and alkaline species was H_2SO_4 > HCl > HNO_3 > NaOH. The only membranes that rejected nitric acid to any extent were asymmetric cellulose acetate (RO-97) and cellulose methyl sulfonate O-propyl sulfonic acid (211-96B). None rejected sodium hydroxide.

3. The β-glucan acetate dimethylaminoethyl ether did not reject any of the acids or base.

During the testing with the acidic solutions, the water fluxes of the seven membranes remained stable at their 20-hour values. However, when the sodium hydroxide solution was tested, the fluxes of the five ultrathin membranes increased three to eight times, and the flux of the

Table 15. Rejection of Acids and Bases by Membranes During Reverse Osmosis Testing

Test Conditions:

Temperature. . . . . 25°C
Pressure . . . . . 600 psig
Flow Rate. . . . . 1650 ml/min
Feeds. . . . . H_2SO_4 and 100 mg/l Zn^{++} at pH 2.4
0.1N H_2SO_4 -- pH 1.5
0.1N HCl -- pH 1.2
0.1 N HNO_3 -- pH 1.2
0.1N NaOH pH 11.8

Membrane	Percent Rejection Based on pH					pH of Product Water				
	H_2SO_4 & Zn^{++}	H_2SO_4	HCl	HNO_3	NaOH	H_2SO_4 & Zn^{++}	H_2SO_4	HCl	HNO_3	NaOH
Cellulose Acetate (E 398-10)	96 ± 3	84 ± 3	37 ± 17	0	0	3.8	2.3	1.4	1.2	11.8
Cellulose Acetate (E 360-60)	84 ± 3	37 ± 3	20 ± 17	0	0	3.2	1.7	1.3	1.1	11.8
Asymmetric Cellulose Acetate (RO-97)	99 ± 1	94 ± 1	75 ± 5	37 ± 17	0	5.5	2.8	1.8	1.4	11.7
Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-89A)	98 ± 1	90 ± 2	60 ± 5	0	0	4.2	2.5	1.6	1.2	11.8
Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-96B)	98 ± 1	92 ± 2	75 ± 5	20 ± 17	0	4.1	2.6	1.8	1.3	11.8
β-glucan Acetate Dimethylaminoethyl Ether (211-40A)	0	0	0	0	0	2.4	1.4	1.2	1.1	11.8

asymmetric membrane decreased by half. This performance would indicate that the membranes were not degraded by any of the acidic solutions during the testing period and substantiates earlier evidence that these membranes are rapidly hydrolyzed by alkaline conditions.

The poor rejection performance of these membranes toward several of the acidic species was not necessarily a detrimental aspect of their overall performance. Consider a situation in which a waste zinc sulfate solution containing sulfuric acid was to be treated by reverse osmosis to recover the zinc and not the sulfuric acid. The β-glucan acetate dimethylaminoethyl ether would be the ideal membrane to perform this task, since it could retain over 98 percent of the zinc salt and would allow passage of the acid. In similar situations where all, part, or none of the acid was to be recovered, a suitable membrane could be chosen to do the job.

Test Variables Affecting Membrane Performance

The reverse osmosis performance of a membrane is not only dependent on the chemical and physical nature of the membrane itself, but also on the conditions under which the testing is performed. These conditions include operating pressure, operating temperature, and pH of the feedwater.

Operating Pressure

Studies of the effects of operating pressure on the water flux of a membrane showed that one distinct advantage to be gained by increasing the pressure was an increased water flux.[8] The results of these studies are plotted in Figure 8.

The ratios of the water flux at 1000 psig to that at 200 psig were calculated and are given below.

1) Asymmetric cellulose acetate (RO-89). 3.5

2) Ultrathin cellulose acetate (E 360-60). 4.5

3) Ultrathin cellulose methyl sulfonate O-propyl sulfonic acid (211-89A) 4.3

4) Ultrathin cellulose acetate (E 383-40). 4.8

5) Ultrathin β-glucan acetate dimethylaminoethyl ether (211-40A) 4.9

6) Ultrathin cellulose methyl sulfonate O-propyl sulfonic acid (211-96B) 4.8

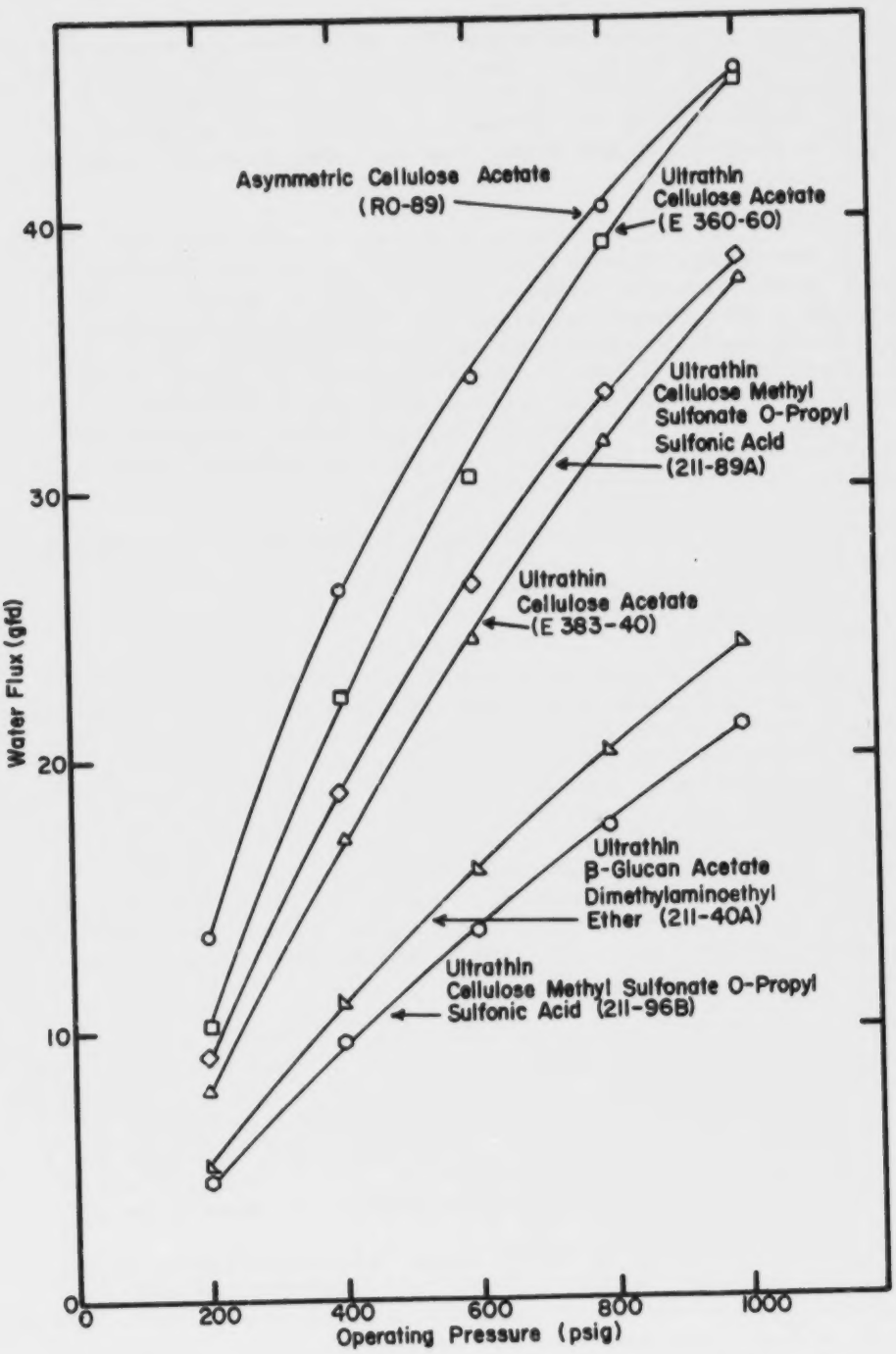


Figure 8. Effect of Operating Pressure on the Water Flux Behavior of Reverse Osmosis Membranes

For the ultrathin membranes, the water flux at 1000 psig averages 4.7 times that obtained at 200 psig. However, the ratio of fluxes for the asymmetric membranes was lower (3.5). This lower ratio could be a result of the compaction of the porous substrate of the asymmetric membrane. The increase in the water flux over this pressure range was not linear.

Previous tests with highly concentrated copper sulfate solutions (20,000 to 40,000 mg per liter, copper) indicated that to obtain adequate water fluxes, the operating pressure should be 600 psig or greater. These higher pressures were needed to offset the flux-diminishing effects of osmotic pressure while still maintaining an acceptable water flux across the membrane. Of course, any advantages to be gained by increasing the pressure must be balanced against the disadvantages of such an increase. These disadvantages include higher equipment and operating costs and water flux declines caused by membrane compression and concentration polarization.

Increases in the pressure had little effect on the metal ion rejection of the membrane.

Operating Temperature

Studies of the effects of operating temperature on the water flux of six membranes showed an initial increase in water flux with increasing temperature.[8] The results of these studies are plotted in Figure 9. A temperature increase from 25°C to 45°C increased the water flux by a factor of 1.4 (average). However, after the temperature exceeded 45°C, a drop in the water flux occurred for four of the six membranes. This was probably caused by an annealing of the membranes by the high temperature. Annealing, like air drying, reduces the water flux of a membrane. It is also an irreversible process. If the temperature were to be returned to a previously tested lower temperature, the water flux of the membrane would be lower than that previously obtained at that temperature.

Figure 10 shows the hysteresis effect on water flux for an ultrathin cellulose acetate membrane (E 360-60) as a function of temperature. The water flux of the membrane was 28 gfd at the initial testing temperature of 25°C. After the membrane was tested at 60°C, it was retested at 25°C and had a water flux of 14.5 gfd. All four membranes whose water flux declined after reaching 45°C behaved similarily. Such behavior would support the conclusion that these membranes had been annealed.

The two membranes for which the water fluxes were not affected by the temperature 1) could have been annealed at a higher temperature prior to testing [as is suspected in the case of the cellulose acetate, (RO-89)], or 2) needed higher temperatures before any significant effects of annealing became evident (as was probably the case with β-glucan

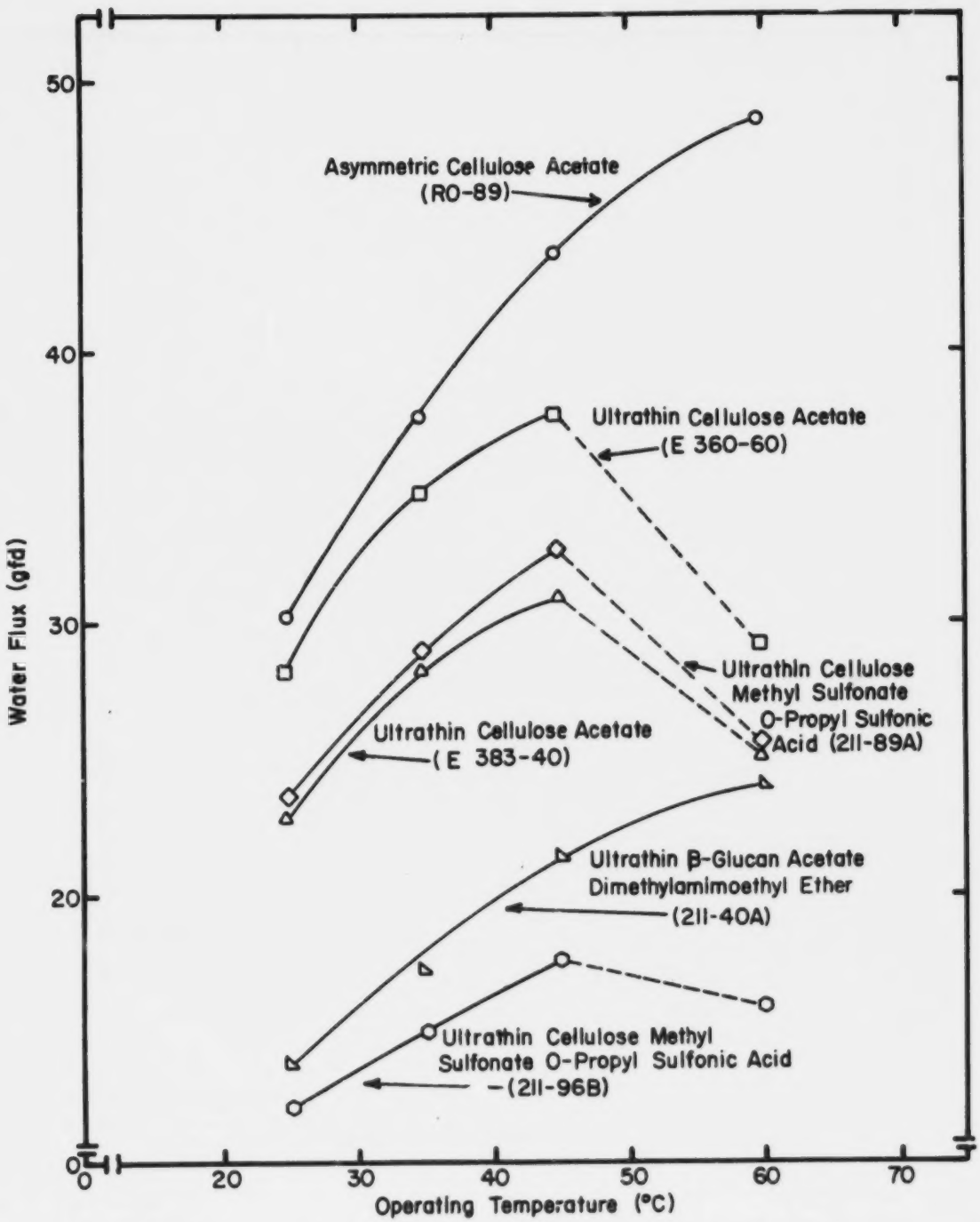


Figure 9. Effect of Operating Temperature on the Water Flux Behavior of Reverse Osmosis Membranes

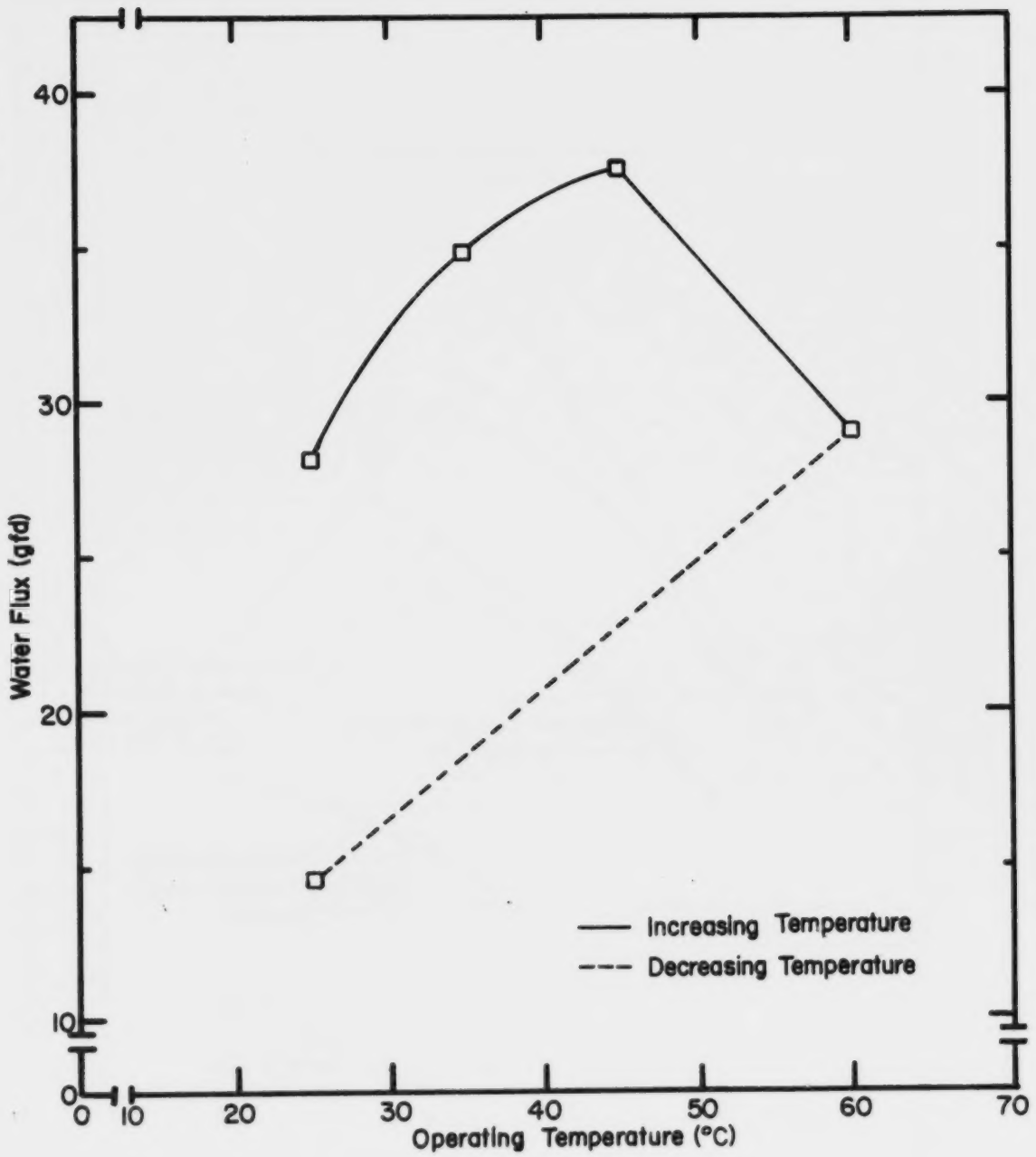


Figure 10. Effect of Operating Temperature on the Water Flux Behavior of an Ultrathin Cellulose Acetate Membrane (E 360-60)

acetate dimethylaminoethyl ether). Ultrathin β-glucan acetate dimethylaminoethyl ether membranes may exhibit higher flux and more stability at higher temperatures compared to the cellulose-derivative membranes.

Increases in the operating temperature caused no significant changes in the metal ion rejection of the membranes.

The above data indicate that if temperatures greater than 25°C are used, membranes (cellulosic) annealed at a temperature higher than the working temperature should be used. Such a situation would occur if it were not economically or physically feasible to reduce the temperature of a warm rinse from a hot plating bath prior to reverse osmosis treatment.

pH Effects

Of all sixteen membranes tested at pH's of 2.5 and 5.0, only one showed any change in reverse osmosis performance with a change in pH. That membrane was β-glucan acetate dimethylaminoethyl ether. A 900-angstrom-thick membrane exhibited a water flux of ∿ 47 gfd at pH 2.5 and a water flux of ∿ 15 gfd at pH 5.0. It was suspected that this pH dependency was a result of the acid-accepting properties of the dimethylamino group.

Optimization of Ultrathin Membrane Systems for Better Reverse Osmosis Performance

The polymers from which the ultrathin membranes are cast can be chemically modified, or the resulting membranes can be physically changed, to obtain optimum reverse osmosis performance. The commercial asymmetric membranes cannot be manipulated in this manner, since they have already been optimized and are ready for use as-is, when purchased. The following tests and explanations, therefore, are concerned only with ultrathin membranes.

The reverse osmosis performance of a membrane can be improved to a considerable extent by modifications in its fabrication process. The membrane variables that can be modified for the highest water fluxes, highest rejections, and lowest flux declines include:

- Polymer preparation process and degree of substitution
- Membrane-annealing conditions
- Membrane thickness
- Type of support film

Controlling the effects of the above variables would improve the performance of the membrane-support composite for optimum treatment of metal finishing wastewaters.

Polymer Preparation and Degree of Substitution

Small differences in the chemical composition of similar membranes can result in large differences in their reverse osmosis properties. In the Eastman cellulose acetate polymer series (which have already been optimized), the E 398-10 polymer, which is 39.8-percent acetate, produces a lower flux and a higher rejection membrane than the E-360-60, which is 36.0-percent acetate. Figure 11 gives the water flux curves for these two membranes at similar thicknesses. The water flux of the E 360-60 membrane with the lower acetyl content (or higher hydroxide content--see Appendix A) had a higher flux (<40 gfd) and lower salt rejection (78 percent) than did the E 398-10 membrane with the higher acetyl content (or lower hydroxide content) which had a water flux of ∿28 gfd and a rejection of 93 percent.

Similar differences for these two membranes were also evident from the reverse osmosis testing of chromic acid. The E 360-60 membrane exhibited a water flux of 30 gfd and a chromium rejection of 75 percent (pH 5.0), and the E 398-10 membrane exhibited a water flux of 18 gfd and a chromium rejection of 94 percent (pH 5.0).

In the previous tests two different ultrathin cellulose methyl sulfonate O-propyl sulfonic acid membranes were evaluated (Table 4). The 211-96B derivative exhibited a water flux of 42 gfd and metal ion rejections of 83 to 99 percent, and the 211-89A derivative exhibited a water flux of 19 gfd and metal ion rejections of 97 to >99 percent. These water flux and rejection differences were caused by the difference in the amount of propyl sulfonic acid substituted on the cellulose unit (degree of substitution -- DS).

The 211-96B formulation for the ultrathin cellulose methyl sulfonate O-propyl sulfonic acid membranes had a slightly higher degree of substitution (as indicated by reaction conditions) than did the 211-89A formulation. This is the basic reason that the 211-96B membrane exhibited higher water flux and lower metal ion rejections than did the 211-89A membrane. By rigorously controlling the reaction conditions during the synthesis of this membrane polymer, it should be possible to prepare a polymer with certain desirable and predictable properties. The investigation and study of the reaction conditions were not within the goals of this screening program.

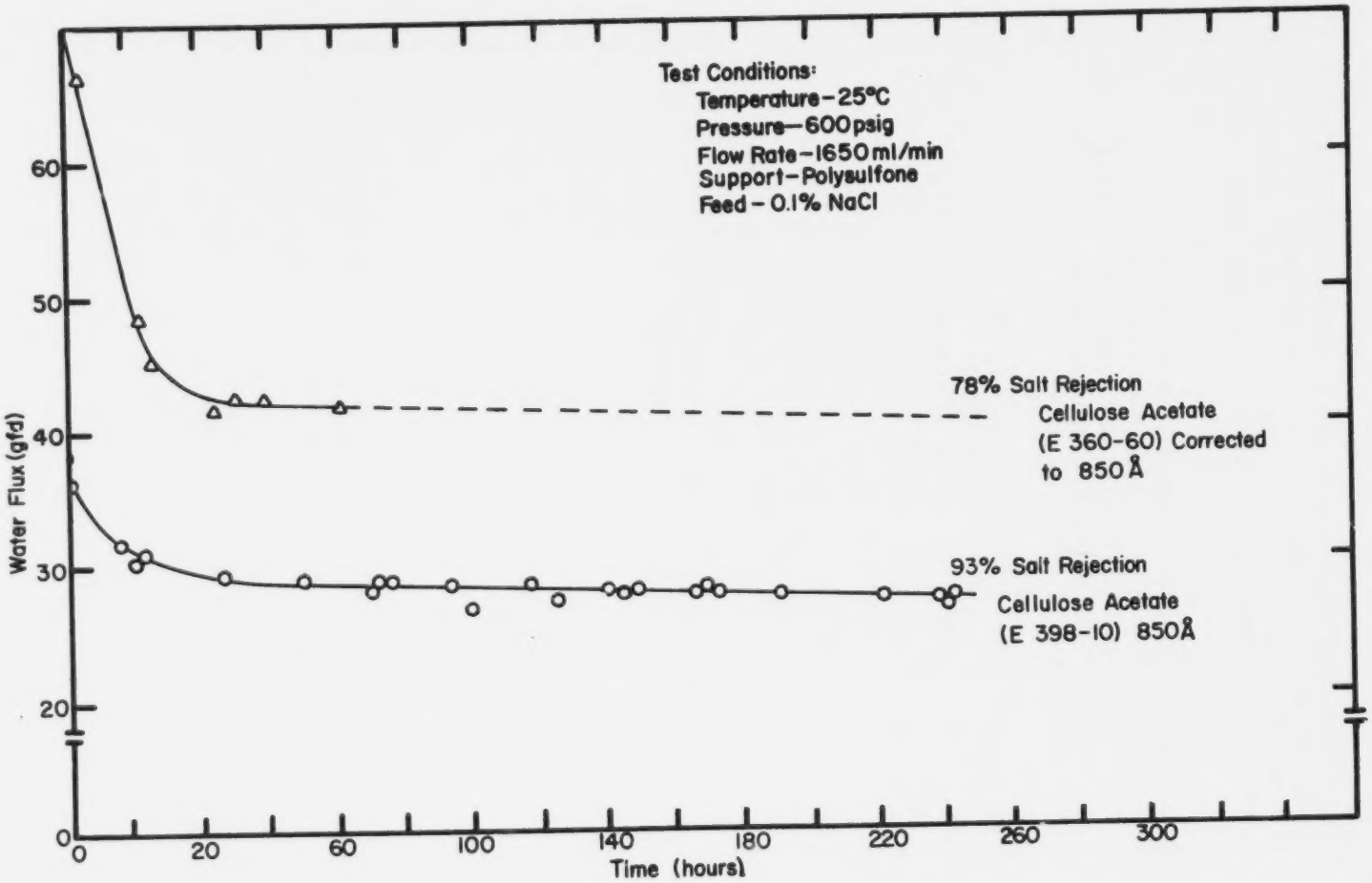


Figure 11. Water Flux Behavior of Two Cellulose Acetate Membranes of Differing Acetyl Content During Testing with 0.1-Percent Sodium Chloride

Annealing

It is well known that heat annealing decreases the flux decline of asymmetric cellulose acetate membranes. It also decreases the water flux and increases the salt rejection. The same effects have been observed with ultrathin membranes when annealed by heat or air drying.

Effect on Water Flux. Figure 12 shows the effect of annealing on the water flux of cellulose methyl sulfonate O-propyl sulfonic acid (211-96B). One membrane was annealed by air drying after being placed on a polysulfone support; the other membrane was tested wet. The annealed membrane exhibited a lower water flux.

Effect on Flux Decline. The effect of annealing (by air drying) on the flux decline of a cellulose methyl sulfonate O-propyl sulfonic acid (211-96B) membrane was significant and is indicated in Table 16. The flux-decline slope for the annealed membrane was zero, but the non-annealed membrane had a flux decline slope of -0.11.

Table 16. Flux Declines for Annealed (air dried) and Nonannealed Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid Membranes

Annealing	Flux Decline*
None	-0.11
Air dried	0.00

*Slopes from logarithmic plots of flux in gfd versus time in hours from 1 hour to 260 hours of testing.

Effect on Salt Rejection. Annealing increased the salt rejection of the cellulose methyl sulfonate O-propyl sulfonic acid (211-96B) membrane from approximately 62 percent (for nonannealed) to 96 percent (Figure 12).

It is possible to control annealing so that the three membrane properties of water flux, flux decline, and rejection are optimum for treating specified types of effluents.

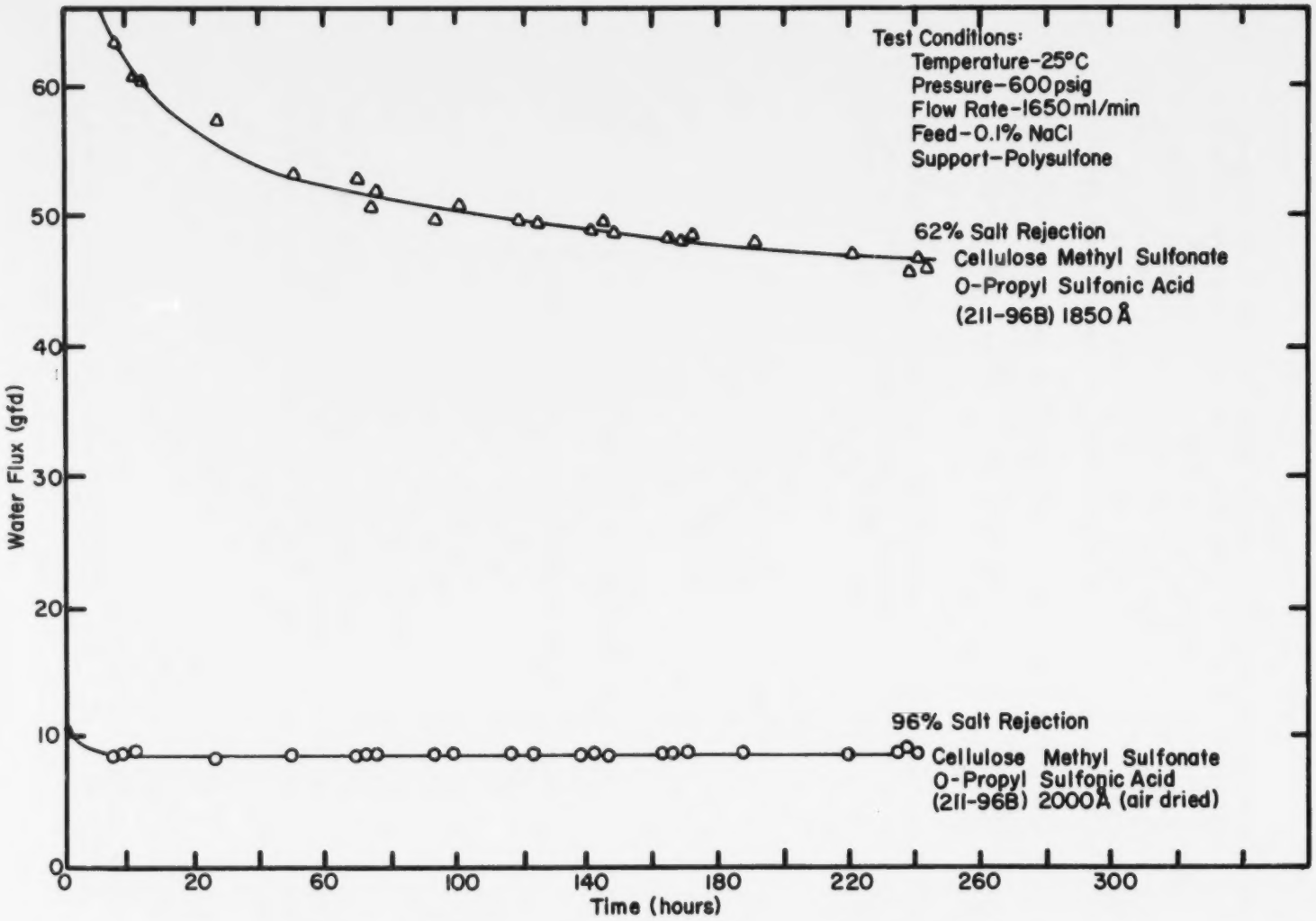


Figure 12. The Effect of Annealing on the Water Flux and Rejection on the CMSOPSA Membranes

Thickness

The solution-diffusion model[9] forms the basis for the flux-versus-reciprocal-thickness plot. A conclusion from this proposed mechanism of transport is that the water flux is equal to a constant term multiplied by the reciprocal thickness and the net pressure driving force. Since the pressure was kept constant for all the tests, a plot of flux versus reciprocal thickness should yield a straight line through the origin with a slope proportional to the constant term.

Figure 13 illustrates the effect of thickness on the water flux of an ultrathin cellulose acetate (E 398-10) membrane. The relationship was linear with inverse thickness over the thickness range studied (400Å to 2000 Å).

Similar thickness-flux relationships were exhibited by the ultrathin cellulose methyl sulfonate O-propyl sulfonic acid (211-89A) during tests with metal salt solutions. Table 17 gives the data from these tests.

Table 17. Thickness and Flux Data for Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-89A)

Membrane Thickness (Å)	70-Hour Water Flux (gfd)
1100	19
530	25
380	27

A plot of the flux versus reciprocal thickness was not linear. This nonlinearity, however, was probably caused by the experimental nature of the membrane, and further development of membrane formation procedures would be expected to linearize the thickness-flux relationship.

Choice of Membrane Support

Because ultrathin membranes are rather fragile, they must be mounted on a support to be used for reverse osmosis. Two membrane supports have been used to date--Millipore VFW filters[10] and polysulfone films. The microporous polysulfone films were developed at North Star and are presently used for the support of ultrathin tubular membranes.[11, 12]

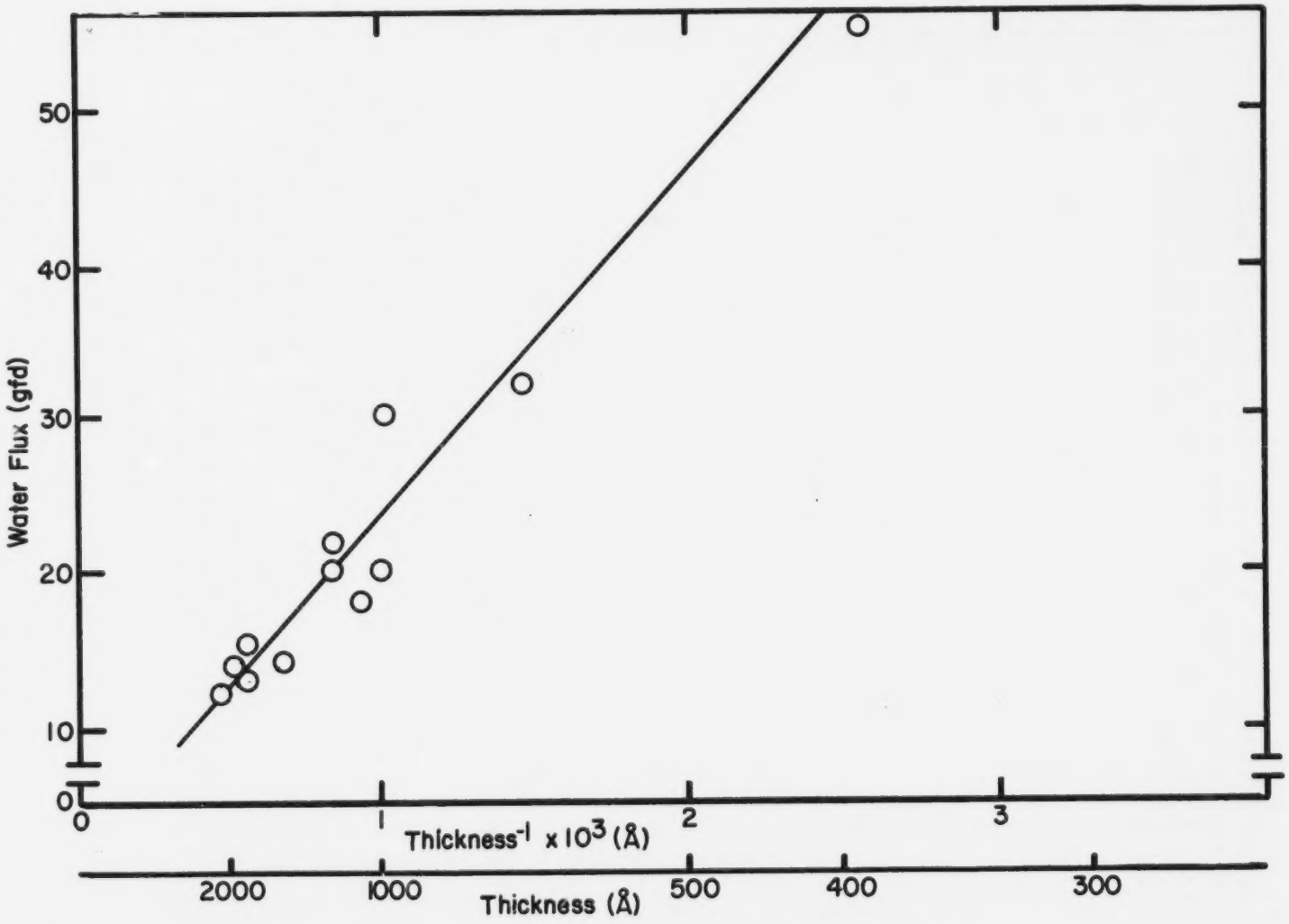


Figure 13. Effect of Membrane Thickness on Water Flux for Cellulose Acetate (E 398-10)

Membranes supported on the polysulfone exihibited lower flux declines than membranes supported on the Millipore filters during a 260-hour test. Flux-decline values from the slopes of logarithmic plots of flux versus time for the cellulose acetate (E 398-10) and cellulose methyl sulfonate O-propyl sulfonic acid (211-96B) membranes on both supports are given in Table 18.

Table 18. Flux Decline Slopes for Ultrathin Membranes on Millipore and Polysulfone Supports in a 0.1-Percent Sodium Chloride Solution

Ultrathin Membrane	Flux Decline*	
	Millipore Support	Polysulfone Support
Cellulose acetate (E 398-10)	-0.08	-0.05
Cellulose methyl sulfonate O-propyl sulfonic acid (211-96B)	-0.14	-0.11

*Slopes from logarithmic plots of flux in gfd versus time in hours from 1 hour to 260 hours of testing.

Polysulfone was chosen for use as the support material for the above-stated reasons as well as for its inertness to acids and bases.[13] The highly alkaline and acidic nature of many metal finishing wastewaters would require the use of a support having this property.

Conclusions

A large number of variables must be manipulated for any membrane optimization. The possibilities of attaining the high water fluxes and rejections and low flux declines that appear achievable with ultrathin membranes make this step necessary. By (1) rigorously controlling the polymer preparation, (2) optimizing the annealing conditions, (3) producing as thin a membrane as practical, and (4) using a polysulfone support film, ultrathin membranes should result which have significantly better reverse osmosis performance than they now exhibit.

SECTION VI

POSSIBLE APPLICATIONS OF REVERSE OSMOSIS TO METAL RINSE SOLUTIONS

The treatment of metal finishing rinse solutions is ideally suited to reverse osmosis technology. These waste rinses are generally (1) toxic, (2) moderate, but steady, in volume, and (3) contain low concentrations of the metal salts and other bath solutes. The present methods for disposing of these wastewaters include lagooning, direct dumping into waterways, and chemical treatment prior to disposal. In many instances, none of these methods of disposal can adequately handle the job. The direct discharge of the toxic wastewaters into rivers and streams can harm aquatic life. Discharge of slugs of highly concentrated wastes into sewers can upset the biological treatment processes. (Table 19 gives some recommended standards for sewer discharges and Appendix F gives the metal concentration in the rinse waters of some common plating baths.) The large volume and rather long reaction times required for chemical treatment require large holding tanks for the wastewaters. The low concentration of the reacting species in the rinse wastewaters also prolongs the time for effective chemical treatment. Even after these wastewaters have been treated, there still remains the problems of disposal of a still-toxic sludge, and water that contains a high concentration of nontoxic salts.

The major advantages of reverse osmosis in treating these rinse waters are that reverse osmosis could not only render any waste effluent harmless to the environment or reusable as purified process water, but also it could permit the recovery of metal and other values discarded in conventional treatment processes.

Treatment of Rinse Waters from a Copper Sulfate Plating Bath

Figure 14 is a diagram of a representative copper plating line. The circled section on this figure encloses the copper sulfate plating bath and the countercurrent rinses. The following discussion considers the application of reverse osmosis to the treatment of these countercurrent rinse waters. Figure 15 is a diagram of this application. The data on bath makeup, drag-out rate, rinse water concentration and rinse rate were taken from Chapter 13 of *Industrial Wastes, Their Disposal and Treatment*.[14] The data on water flux, copper rejection, and the membranes to be used were taken from the experimental work reported in the previous section (Acidic Wastewaters Containing Single Metal Salts). An explanation of each part of this system follows.

Table 19. Recommended Standards for Metal Finishing Waste Concentrations

Sewer Discharge

Component	Typical Limits[15]	Typical Range[16]	New York (1963)
pH	6-10	5-10	--
Ni (mg/l)	2.0	2-10	3.0
Cu (mg/l)	0.3	0-4	5.0
Cr^{+6} (mg/l)	0.05	0-10	0.5
CN (mg/l)	0	0.2	0.2

In Final Electroplating Rinse

Component	Reasonable Concentration Limits[17] (mg/l)
Ni	39
Cu	39
Cr^{+6}	16
CN	39

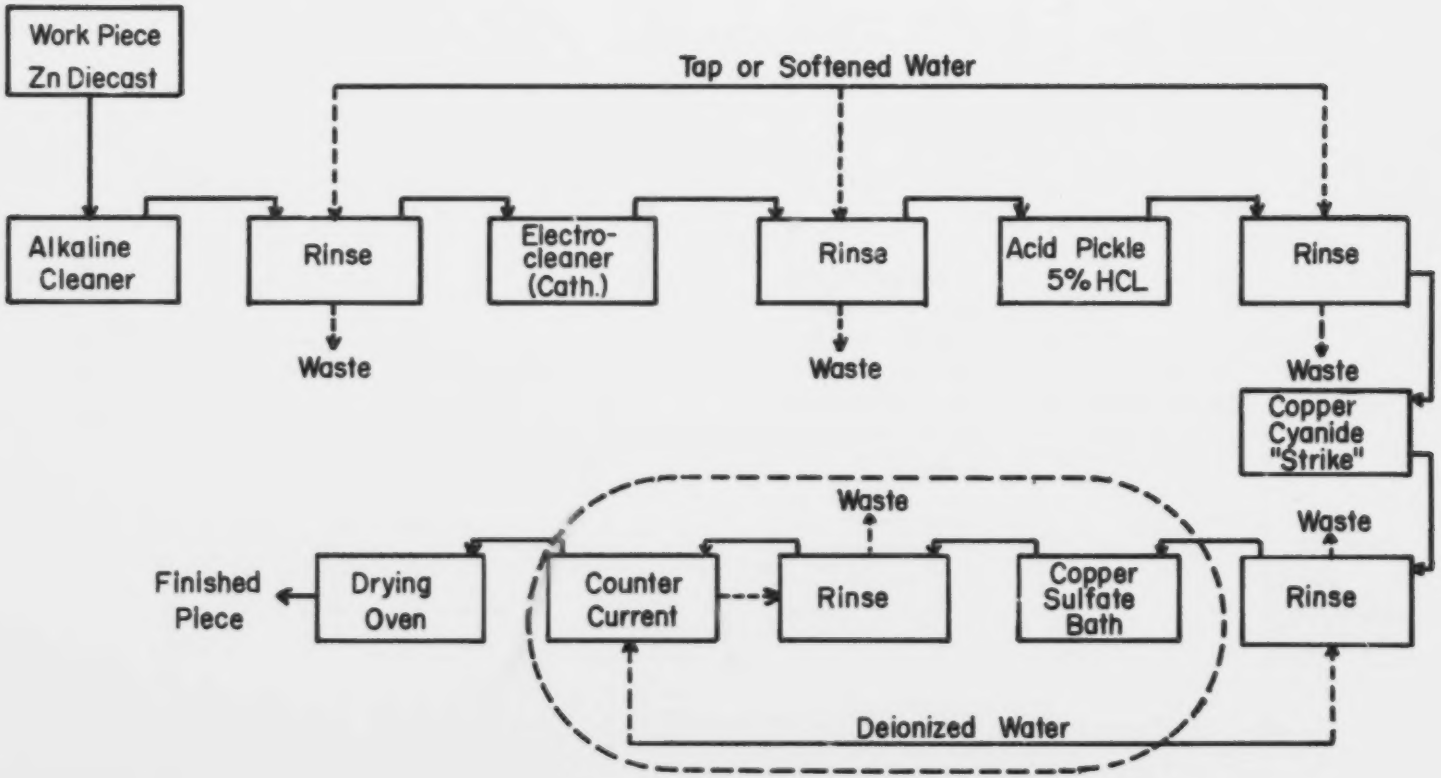


Figure 14. Copper Plating Line

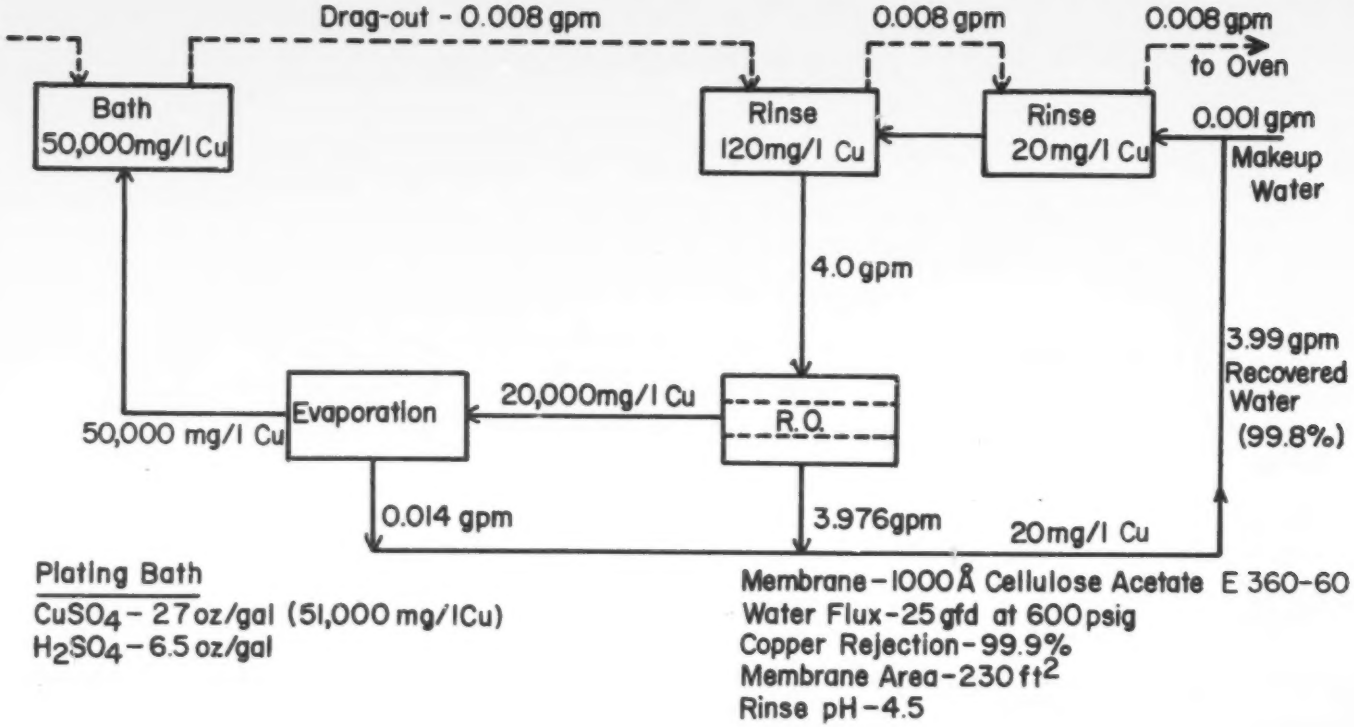


Figure 15. Application of Reverse Osmosis to a Typical Copper Plating Line

Bath Solution

Before a reverse osmosis system can be applied to the treatment of plating rinse waters, the various properties of the plating bath must be considered. These include (1) chemical composition and concentration, (2) acidity or alkalinity, (3) temperature, and (4) rate of evaporation. The first three bath properties will determine the properties of the rinse solution to be treated. The last property will determine the concentration of the reverse osmosis treated feed needed for return to the plating bath. If no evaporation takes place, the concentrated feed solution must be of the same concentration as the bath. If evaporation does occur, the reverse osmosis treated feed can be of a lower concentration than the bath in order to replace water lost during evaporation.

In Figure 15, the bath concentration is approximately 50,000 mg per liter of copper, the solution is acidic, the temperature is 60°F, and the rate of evaporation is negligible. The copper lost from the bath during the plating process is replenished by using copper anodes.

Drag-Out Rate

The drag-out rate is the amount of bath solution being carried by the work piece(s) from the plating bath to the rinse. In Figure 15 the drag-out rate is 0.008 gallons per minute. This is a function of the rate of work-piece throughput, surface area, shape, orientation of the work piece, and drain time. The drag-out rate will determine the metal salt and acid concentration of the rinse waters.

Rinse Water

The concentration of metal salts and other solutes in the rinse water is an important factor in determining the product appearance. Spotting of the piece will result if the concentration of a species is higher than a certain limit. Such an occurrence would require the addition of a polishing step after the piece had been dried.

Table 19 gives a recommended limit for the copper concentration in the rinse of 39 mg per liter. Figure 15 shows that the first rinse solution substantially exceeds this value; thus, the necessity for a second rinse which has a value below the recommended limit.

The countercurrent rinse system used in Figure 15 not only reduces the copper concentration in the final rinse water, but also conserves on the amount of water needed to produce a high-quality product.

Reverse Osmosis System

The overflow of 4.0 gallons per minute from the first rinse in Figure 15 is that which would be treated by reverse osmosis. Figure 15 shows the reverse osmosis system concentrating the 120 mg per liter rinse to 20,000 mg per liter (a 166.5-fold increase) and recovering 3.98 gallons of water per minute. To accomplish this recovery, the entire reverse osmosis system must have the following performance parameters:

- Pressure -- 600 psig
- Membrane water flux -- 25 gfd
- Rejection of copper -- 99.9 percent
- Membrane area -- 230 ft^2
- Membrane -- ultrathin cellulose acetate (E 360-60) at 1000 Å

Reverse Osmosis Retentate

To determine to what degree the rinse water should be concentrated, two factors have to be considered:

1. The effect of osmotic pressure in reducing the water flux;
2. The effect of concentration polarization in reducing the water flux and the copper rejection.

In the case in Figure 15, the rinse water was concentrated to only 20,000 mg per liter of copper because higher concentrations would reduce the flux of the membrane (Factors 1 and 2), requiring more membrane area to treat the waters. Higher concentrations would also cause the copper concentration of the recovered water to increase since the copper rejection of the membrane is constant.

Evaporation

For recycle, the retentate must be of the same concentration as the plating bath. In Figure 15 the reverse osmosis retentate is too low for recycle and must be concentrated further. This is done by evaporation to a concentration of 50,000 mg per liter. The resulting retentate can be returned to the plating bath, and the evaporated and condensed water can be combined with the water from the reverse osmosis system for recycle to the final rinse solution.

Recovered Water

The concentration of the metal salts in the recovered water depends mainly on the rejection of the reverse osmosis membrane and the concentration of the reverse osmosis retentate. In Figure 15 the concentration of copper is 20 mg per liter (or a 99.9-percent rejection of the retentate) and the flow rate is 3.98 gpm for the reverse osmosis unit and 0.01 gpm from the evaporation process. This water, 3.98 gpm, is returned to the final rinse. Additional deionized water 0.01 gpm, must be added to maintain material balance.

Operating Mode -- Reverse Osmosis

The mode of operation used in Figure 15 was a single-pass operation using tubular units to support the membrane. To maintain the volumetric flow rate and velocity in the tubes during reverse osmosis treatment, the cross-sectional area or the number of tubes would have to be reduced in downstream sections of the reverse osmosis system.

The minimum amount of space that would be required by the reverse osmosis tubes alone would be 19.5 cubic feet. This volume would contain approximately 450 1/2-inch (ID) tubes with a total membrane surface of 230 square feet. The dimensions of the tubular unit would be 36 in. by 18 in. by 51 in. This calculated volume was based on the use of American Standard TM 4-14 tubular modules (14 tubes per module, 51-inches module length, 4-1/2-inch module diameter and 7.28 square feet of membrane area).

Results

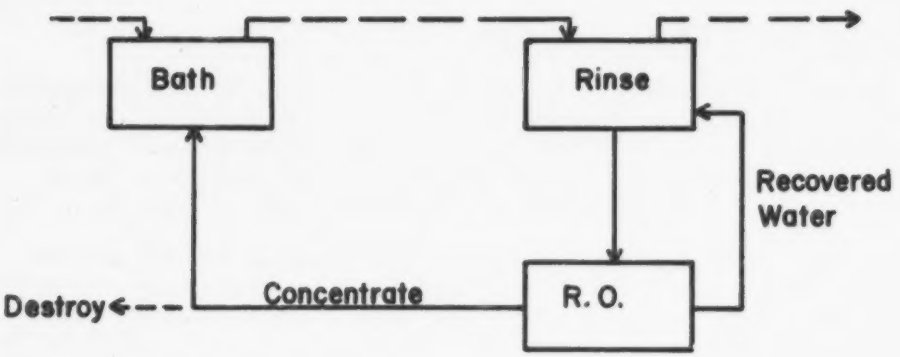
The recovery of the copper salts and water is given below.

	With RO	Without RO
Makeup deionized rinse water	0.01 gpm	4.0 gpm
Water recovered for reuse	99.8%	0%
Copper sulfate recovered for reuse	99.9%	0%

Alternative Treatment Systems

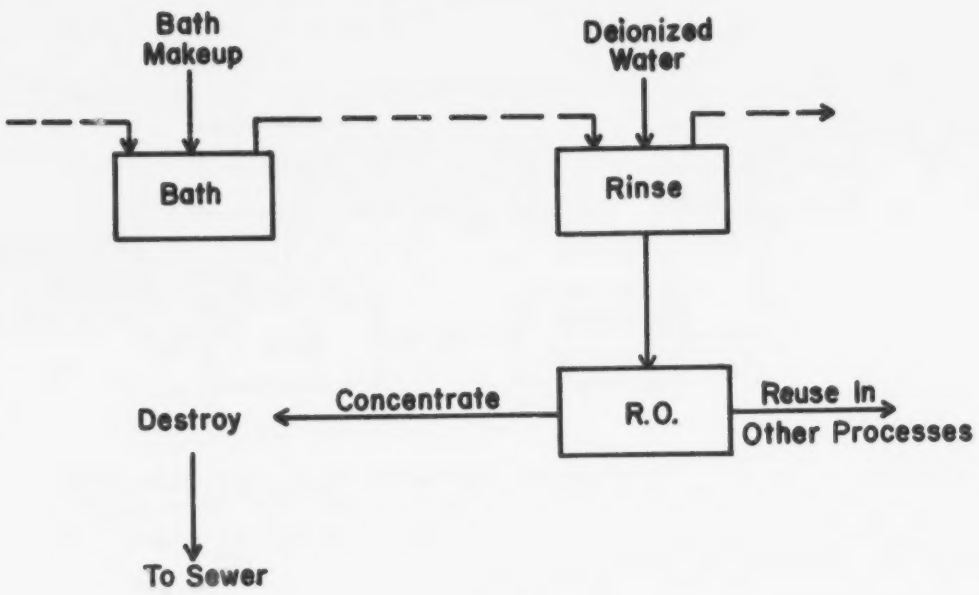
Several other potential applications for reverse osmosis in treating metal finishing wastewaters are given below. In Systems I and II reverse osmosis is used exclusively, and in Systems III and IV, a secondary method of treatment is used in conjunction with reverse osmosis.

System I



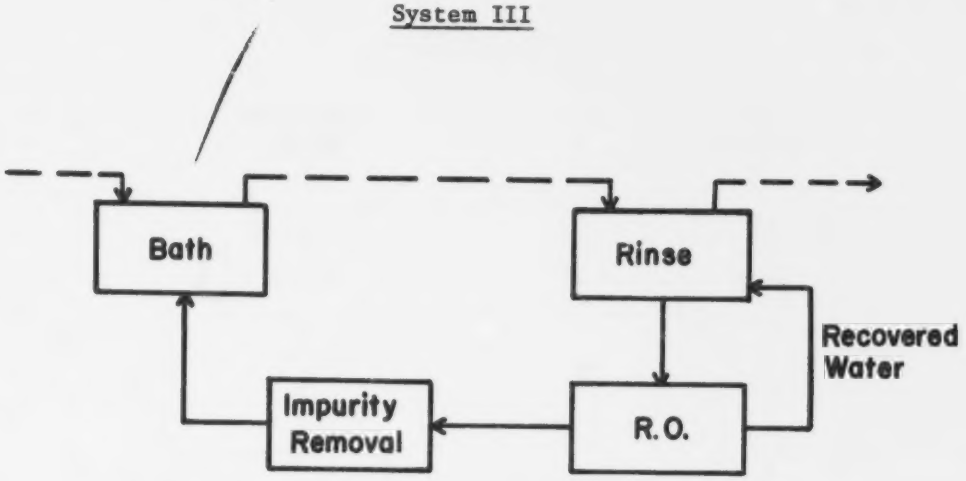
This can be operated as an open or closed system. If the concentrate is contaminated with foreign materials which were brought into the plating bath by the work piece, it cannot be recycled back to the bath (the contaminant would buildup). It should, therefore, be destroyed by a conventional treatment process. If no foreign materials harmful to the bath are present, the concentrate can be recycled.

System II



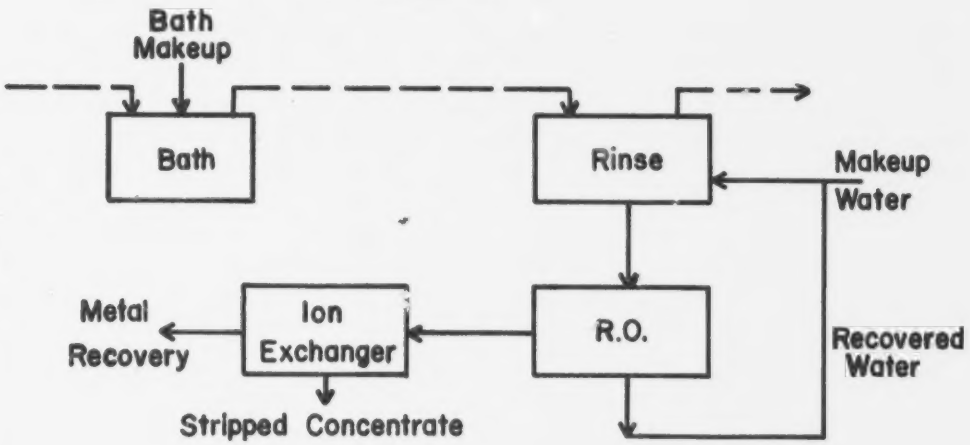
In this system, reverse osmosis is used to treat the wastewater to obtain a concentrate for conventional disposal and recovered waste for reuse in other plant processes. It would be necessary to divert the water to other processes if the metal and other solutes were too high for the final rinse, but low enough for use in cleaning or pickling or other rinse systems in the industrial plant.

System III



A purification unit is added to the system to remove any impurities from the concentrate which might harm the plating bath if recycled. This can be appreciably more practical when treating the higher concentration achieved by reverse osmosis.

System IV



This system is used to recover the water and precious metals in the concentrate. All other solutes are drained into the sewer, or, if toxic, chemically destroyed. One such application could be the recovery of gold from the plating of electronic components.

SECTION VII

ACKNOWLEDGEMENTS

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SECTION VIII

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SECTION IX

APPENDICES

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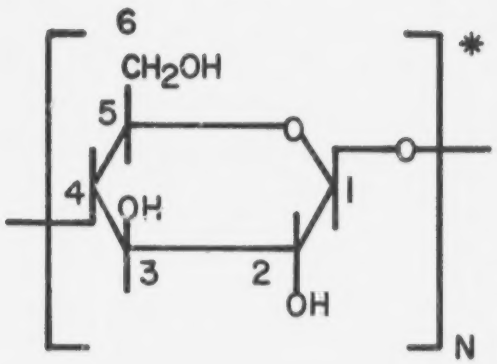
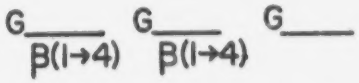
A. Chemical Structures

Cellulose



The chain structure may be represented as:



Where G = anhydroglucose unit

Cellulose Acetate

In cellulose acetate polymers the hydrogen atoms on the hydroxyl groups at positions 2, 3, and 6 of the anhydroglucose unit are partially or completely (cellulose triacetate) substituted by acetate groups. The total degree of substitution (DS) is therefore three, and the various membranes differ with respect to the DS.[1] The proportion of acetyl or hydroxyl groups on the three commercial cellulose acetate polymers is given at the top of the next page.

*This is a modified Haworth formula. The hydrogen atoms attached to the ring carbon atoms are not labeled. The pyran rings are not planar as shown, but are deformed into a "chair" type of structure.

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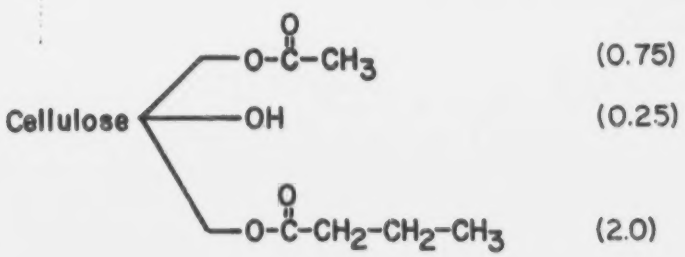
Polymer Designation	Substituted Groups	D.S.
Cellulose Acetate (E 398-10)	OH	0.6
	OAc*	2.4
Cellulose Acetate (E 383-40)	OH	0.7
	OAc	2.3
Cellulose Acetate (E 360-60)	OH	0.9
	OAc	2.1

*Ac = $-\overset{\overset{O}{\|}}{C}-CH_3$

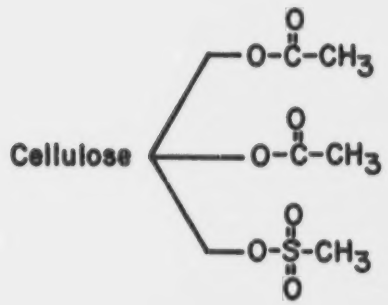
Other Cellulose Derivatives

The cellulosic polymers which contain functional groups other than ethyl acetate or hydroxide are depicted below. The DS of each substituted group, where known, is given. The groups are substituted on the 2, 3, and 6 positions of the anhydroglucose unit.

Cellulose Acetate Butyrate (EAB 171-15)[2]



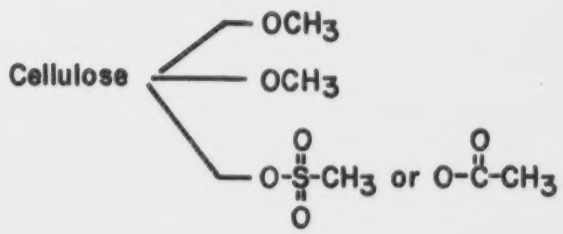
Cellulose Acetate Methyl Sulfonate (211-10C)



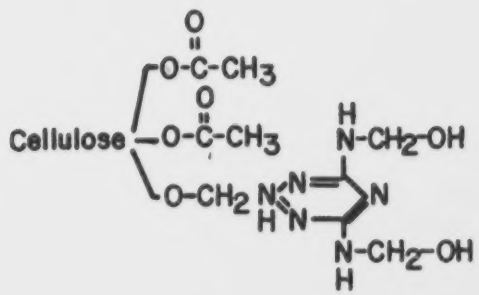
(2.1)

(0.9)

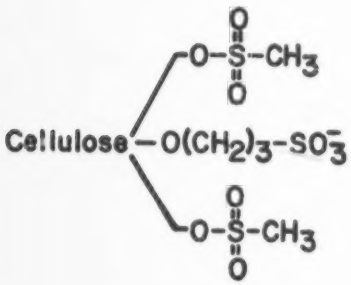
Methyl Cellulose Methyl Sulfonate Acetate



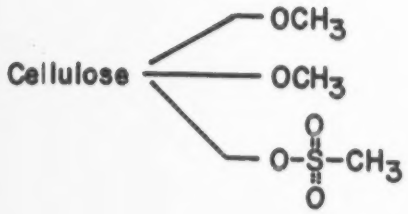
Cellulose Acetate Melamine Formaldehyde Adduct



Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid

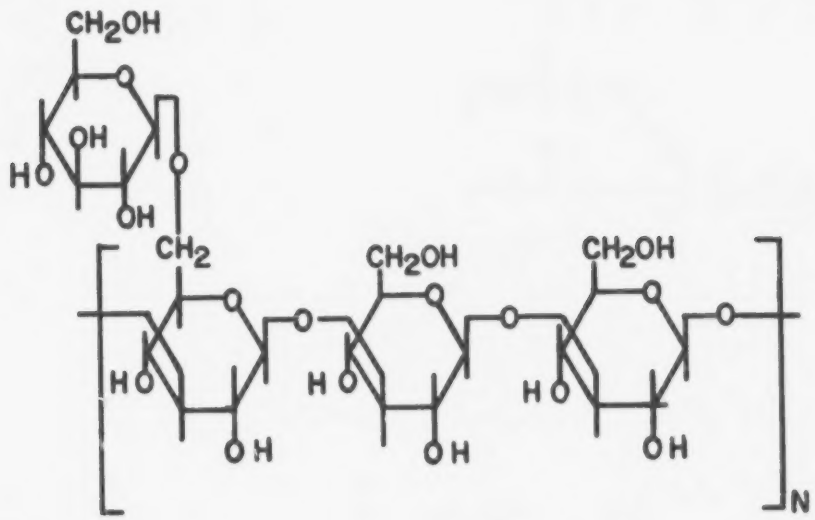


Methyl Cellulose Methyl Sulfonate



Non-Cellulose Polymers

Structure of β-Glucan



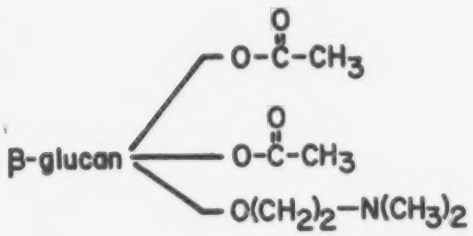
All glucose units are linked beta (1→3) in the chain skeleton and beta (1→6) in the appended glucose units. The chain structure may be represented as:

$$\overset{G}{\underset{G}{\overset{|}{\beta(1\rightarrow 6)}}}\underset{\beta(1\rightarrow 3)}{\overline{\qquad}}\ G\underset{\beta(1\rightarrow 3)}{\overline{\qquad}}\ G\underset{\beta(1\rightarrow 3)}{\overline{\qquad}}\ \overset{G}{\underset{G}{\overset{|}{\beta(1\rightarrow 6)}}}\underset{\beta(1\rightarrow 3)}{\overline{\qquad}}\ G---$$

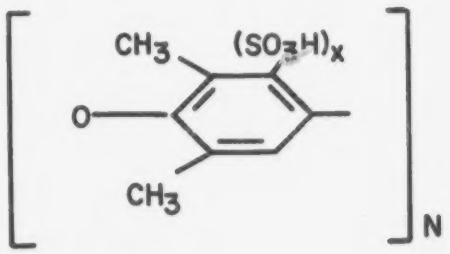
where

G = anhydroglucose unit

The chemical structure of β-glucan acetate dimethylaminoethyl ether is represented as:



Sulfonated Polyphenylene Oxide (JEPDM-127)[3]

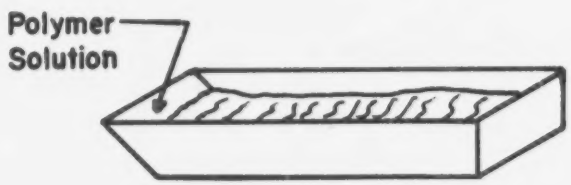


where x is 0.3 to 0.5.

B. Casting Procedures

Casting Ultrathin Membranes[4]

Approximately 0.5 cc of a five-percent (W/W) solution of the polymer in cyclohexanone was placed on the sloped side of a pan partly filled with water, as shown in the sketch below.



As the solution reached the water it spread spontaneously across the surface. When this spontaneous spreading stopped, the membrane was drawn by hand to obtain the desired thickness. The thickness was controlled by the rate of spreading. The cast film remained on the water surface for several minutes to allow the solvent to diffuse into the water and air. The membrane was cut to size with scissors and a wetted support was brought up underneath the floating membrane. The membrane-support composite was removed from the water and placed directly in the reverse osmosis cell.

Casting Polysulfone Supports[5,6]

Polysulfone resin (30 g Union Carbide Bakelite P-3500) was added slowly to 170 g of dimethylformamide, with rapid stirring, and heated to 100°C to give a clear solution. The casting was performed in a room maintained at below 20-percent relative humidity. The polysulfone casting solution was spread on a glass plate using a Gardner casting knife with a four-mil clearance. The plate was quickly immersed in water to gel the film which then floated free from the glass plate. The air surface (glossy side) of the film was used to support the membrane.

C. Polymer Synthesis

Cellulose Acetate Methyl Sulfonate (211-10C)

Ten grams of Eastman cellulose acetate E 360-60 were dried at 105°C for two hours and dissolved in 140 ml of pyridine. After cooling the solution to -10°C, 10 g of methane sulfonyl chloride in pyridine were added in small portions. The solution was stirred for 24 hours at room temperature and precipitated into cold water. The precipitate was dispersed in the water in a Waring Blendor, filtered, and dried at 60°C. The product (13 g) was soluble in cyclohexanone and was estimated to have an acetyl degree of substitution (DS) of 2.1 and a methane sulfonate DS of 0.9.

Methyl Cellulose Methyl Sulfonate Acetate (211-69A)

Ten grams of 15 cps viscosity grade methyl cellulose were added to 200 ml of glacial acetic acid. To this solution was added 10 g of methyl sulfonic acid, followed by 50 ml of acetic anhydride. The solution was mixed for two hours. The resulting yellow solution was precipitated in water containing sodium acetate. The precipitate was dispersed in a Waring Blendor, filtered, washed with water, and air dried. The product (12 g) was soluble in cyclohexanone.

β-Glucan Acetate Dimethylaminoethyl Ether (211-40A)

Ten grams of β-glucan (Pillsbury purified grade) was dispersed in 100 ml of 20-percent NaOH. Five grams of 2-dimethylaminoethyl chloride hydrochloride were added, and the solution was mixed for 24 hours at room temperature. The etherified product was precipitated in a liter of methanol, filtered, and washed with methanol and glacial acetic acid. This product was dispersed in 180 ml of glacial acetic acid. Two ml of 70-percent perchloric acid were then added, followed by 50 ml of acetic anhydride. After a few minutes, the resulting hazy solution was precipitated in water containing sodium acetate, filtered, washed with water, and air dried. The product (13 g) was soluble in cyclohexanone.

Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-89A)

Ten grams of cotton linters (Hercules A-2000) were swelled in 100 g of 20-percent NaOH at -10°C for 24 hours. Three grams of propane sultone were blended with the wet fiber using a spatula. The mixture was stirred occassionally for six hours, then allowed to stand at room temperature for four days. The etherified fiber was washed with methanol, 2-percent sulfuric acid, and glacial acetic acid.

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The fiber was then dispersed in 250 ml of glacial acetic acid. Twenty grams of methane sulfonic acid followed by 50 ml of acetic anhydride were added to produce a clear, thin solution within 20 minutes. The product was precipitated in 1.5 liters of deionized water containing 20 g of sodium acetate. The precipitate was mixed for 1/2 hour to decompose excess acetic anhydride, chopped in a Waring Blendor, washed, and dried at 100°C. The product (17 g) was soluble in hot cyclohexanone.

Cellulose Methyl Sulfonate O-Propyl Sulfonic Acid (211-96B)

The reaction was performed as above except that: 1) 18 g of cotton linters were reacted with 6 g of propane sultone; 2) the amount of methane sulfonic acid was increased to 25 g; and 3) the reaction time with the methyl sulfonic acid was two hours rather than twenty minutes.

Cellulose Acetate Melamine Formaldehyde Adduct (211-29B)

Ten grams of cellulose acetate (Eastman 398-10) were dissolved in 100 g of dimethylformamide. Twenty grams of trimethylol melamine (American Cyanamide Parez 607) were added, resulting in a clear solution. The solution was heated for 30 minutes at 130°C, evolving formaldehyde vapors. The product was isolated by precipitation in water, filtered, washed, dried at 60°C. It gave a milky-appearing solution in cyclohexanone.

Methyl Cellulose Methyl Sulfonate (211-19A)

Five grams of 100 cps viscosity grade methyl cellulose were dissolved in 100 ml of glacial acetic acid. Fifty milliliters of acetic anhydride and 0.1 gram of 70-percent perchloric acid were added and mixed for five minutes to give a clear solution. The solution was poured into a 0.5-percent sodium acetate solution. The precipitate (6.0 g) of methyl cellulose acetate was dispersed in a Waring Blendor, filtered, washed, and air dried.

Three grams of the dried product were stirred in 100 ml of dioxane and 20 g of methane sulfonyl chloride were added. The product was precipitated in a 0.5-percent sodium acetate solution, filtered, washed, and dried.

D. Analytical Procedures

Metal Ion Concentration

The feed water was made up to the desired concentration of metal ion by dissolution of the following salts in approximately 18 liters of de-ionized water. Higher concentrations were prepared by multiplying these amounts by the appropriate factor.

Salt	Amount (g)	Metal Conc. (mg/l)
$NiSO_4 \cdot 6H_2O$	8.06	100
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	12.69	100
$CuSO_4 \cdot 5H_2O$	7.09	100
CrO_3	3.47	100
$ZnSO_4 \cdot 7H_2O$	7.90	100
CuCN	26.00	18,450

To accurately determine the metal ion concentration in the feed water and product water, analyses for the appropriate ion were made using atomic absorption spectrophotometry.[7] Each time samples of the product water (20 ml) were collected, a sample of the feed water (20 ml) was also collected. The average deviations in measuring the metal ion concentration are listed below.

Range of Measurement (mg/l)	Average Deviation (mg/l)
0 to 2	$\pm$0.02
0 to 10	$\pm$0.05
0 to 100	$\pm$0.5
0 to 1000	$\pm$5.0

The analyses were made with a Varian-Techtron AA-120 Atomic Absorption Spectrophotometer using an air-acetylene flame. Measurements were recorded on a Beckman ten-inch linear recorder.

Ultrathin Membrane Thickness

After the ultrathin membrane had been cast (see Appendix B), a one-inch-square portion adjacent to the portion used for the reverse osmosis studies was removed and placed on a black opaque glass plate and air dried. The thickness was then measured by interferometry techniques using a Reichert Metallograph equipped with a Normaskii polarization interferometer.[4]

Salt Rejection by Conductivity

The rejections of sodium chloride feed solutions were determined by conductivity measurements. The instrument used was a Leeds and Northrup Co. multipurpose electrolytic conductance/resistance conductivity bridge equipped with an Industrial Instruments (Beckman) conductivity cell (G 10Y116).

Acid-Base Rejection by pH Measurements

The rejection of acidic or basic species was calculated from pH measurements according to the following equations:

$$\% \text{ Rejection } (H^+) = 1 - \frac{\text{antilog } pH_f}{\text{antilog } pH_p}$$

$$\% \text{ Rejection } (OH^-) = 1 - \frac{\text{antilog } (14 - pH_f)}{\text{antilog } (14 - pH_p)}$$

where:

f = feed water

p = product water

These measurements were made on a Beckman pH meter, Model 76.

Water Flux

The rate of water passage through the membrane was measured using a graduated pipette which was placed at the product water outlet in the reverse osmosis cell. The rate of flow in ml per minute was determined and multiplied by the factor 21.2 gal·day/ml·ft^2 to obtain the membrane water flux in gal/ft^2 · day.

E. Reverse Osmosis System

The reverse osmosis test loop pictured in Figure E-1 contained a 20-liter reservoir, a Model 241-144B Milton Roy Pump, an accumulator (surge tank), a heat exchanger, six stainless steel test cells, a 100-mesh, high-pressure filter, a needle valve for system pressure control, and a Rotameter-type flow meter.

The design of the test cell is shown in Figure E-2. The cell was machined from AISI 316 stainless steel. Mechanical support for the membrane was supplied by a two-inch-diameter sintered stainless steel plate, 1/4-inch thick. The porous support film was placed between the porous plate and the membrane to protect the membrane from the rough surface of the plate. A seal was obtained with a 1.75-inch (I.D.) "O" ring. The two end plates were held together by four nuts.

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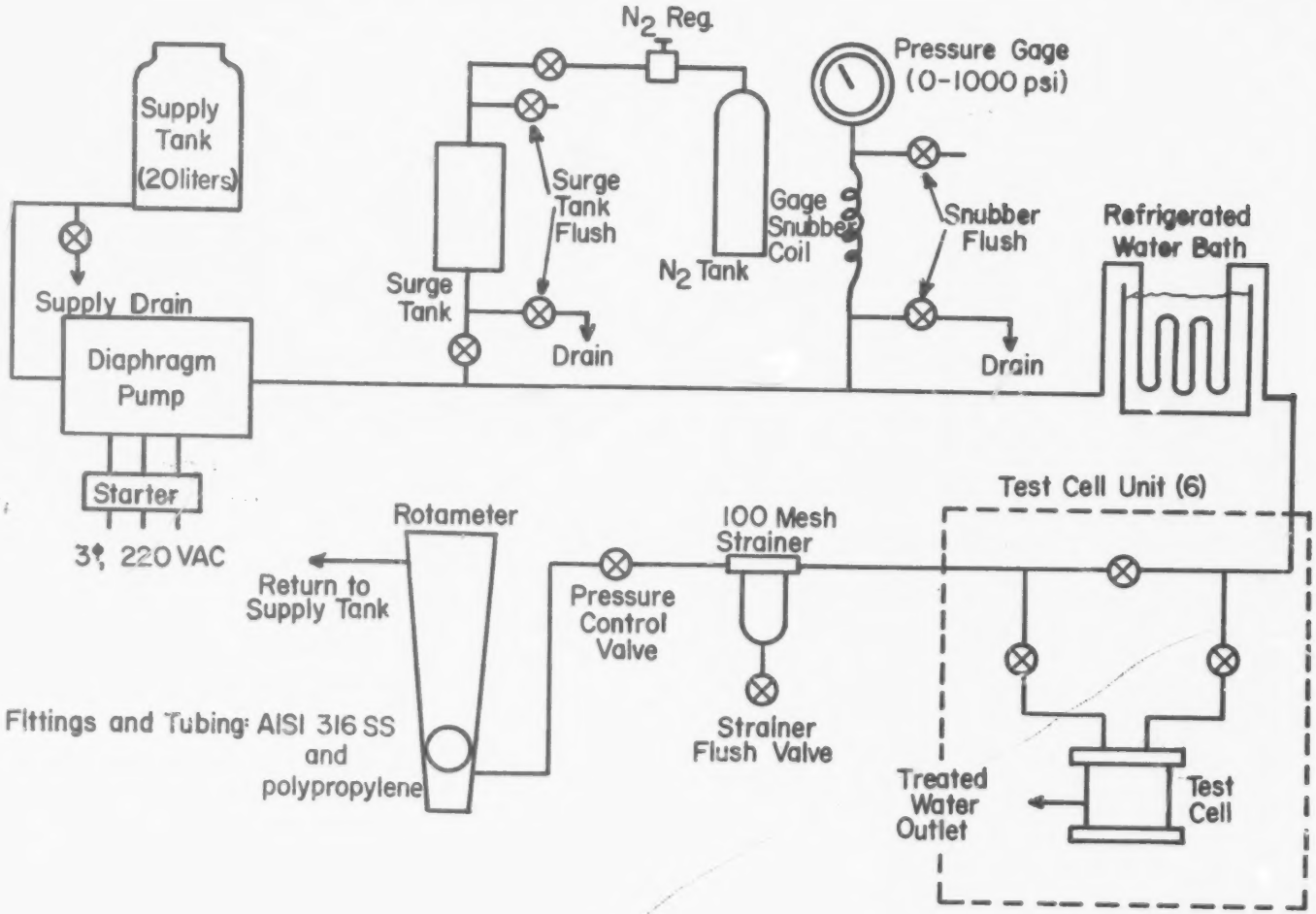

Figure 1. Schematic Diagram of Reverse Osmosis Test Apparatus

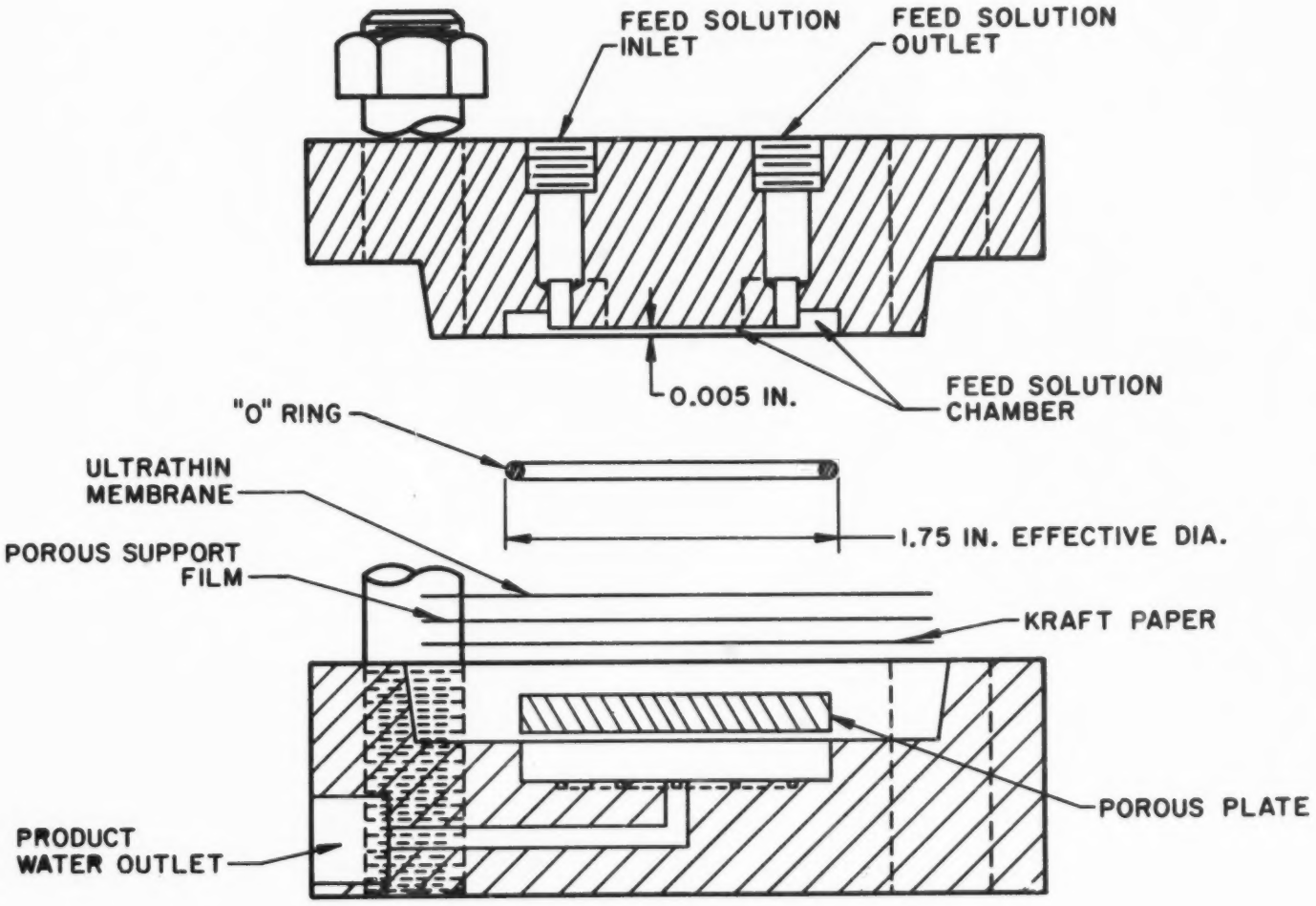

Figure 2. Dynamic Cell for Reverse Osmosis

F. Common Plating Baths

Bath Formula and Plating Conditions(8)	Metallic and Cyanide Concentration (mg/l)	Rinse Concentration (mg/l)*
Nickel 44 oz/gal nickel sulfate (hexahydrate) 6 oz/gal nickel chloride (hexahydrate) 5 oz/gal boric acid pH 1.5 to 4.5 current density 25 to 100 amp/ft^2 temperature 115 to 140°F	75,000 Ni	156 Ni
Copper (acidic) 27 oz/gal copper sulfate (pentahydrate) 6.5 oz/gal sulfuric acid current density 20 to 50 amp/ft2 temperature 60 to 120°F	51,500 Cu	108 Cu
Copper (alkaline) 3.5 oz/gal copper cyanide 5.9 oz/gal sodium cyanide 0.5 oz/gal sodium hydroxide pH 12 current density 20 to 50 amp/ft^2	19,000 Cu 31,000 CN	40 Cu 65 CN
Zinc 24.0 oz/gal zinc sulfate (heptahydrate) 6.0 oz/gal sodium acetate pH 3.0 to 4.5 current density 100 to 300 amp/ft^2 temperature 80 to 120°F	41,000 Zn	85 Zn
Chromium 33.0 oz/gal chromic acid 0.33 oz/gal sulfuric acid	130,000 Cr	270 Cr
Iron 48 oz/gal ferrous ammonium sulfate (hexahydrate) pH 2.8 to 5.0 current density 20 amp/ft^2 temperature 75°F	50,500 Fe	106 Fe

*Based on 0.5 gph drag-out and 4 gpm rinse rate.

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References for Appendices

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5 Organization

Minnesota Pollution Control Agency
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6 Title

Ultrathin Membranes for Treating Metal Finishing Effluents by Reverse Osmosis

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*Treatment of metal finishing wastewaters, *Ultrathin polymer membranes, *Laboratory study, Metal salts, Electroplating wastes, Cleaning and Pickling wastes

27 Abstract

Reverse osmosis has been examined as a process for treating metal finishing wastewaters. Seventeen different membranes were evaluated for the separations of heavy metal ions, acids, bases, and cyanides from water. They included commercially available asymmetric membranes (approximately 0.002 inch in thickness) and ultrathin membranes (1×10^{-6} to 2×10^{-5} inch in thickness). Experimental results showed that reverse osmosis is feasible and effective in treating these effluents for both pollution control and metal ion and water recovery for possible recycle. Although no one membrane was found effective for all effluents, membranes of five different polymers showed considerable promise.

Simulated acidic nickel, iron, zinc, and copper plating bath rinses were effectively treated by ultrathin membranes of three polymers: cellulose acetate, cellulose methyl sulfonate O-propyl sulfonic acid, and B-glucan acetate dimethylaminoethyl ether. Simulated chromic acid rinses were effectively treated by ultrathin cellulose methyl sulfonate O-propyl sulfonic acid. The sulfonated polyphenylene oxide was the only membrane to withstand hydrolysis for over 170 hours by a highly alkaline (pH 11.4) copper cyanide solution. Preliminary engineering considerations on the application of reverse osmosis to the treatment and recycle of rinse waters from an acidic copper (sulfate) plating bath are included.

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